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RESEARCH PAPER RP966

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HEATS OF COMBUSTION OF THE LIQUID NORMAL PARAFFIN HYDROCARBONS FROM HEXANE TO DODECANE

By Ralph S. Jessup

ABSTRACT

The measurements were made by means of a bomb calorimeter, which was calibrated electrically for some of the measurements, and by burning standard sample benzoic acid for the remainder. The samples of liquid were inclosed in thin-walled glass bulbs which were flattened on opposite sides, and were ignited by an electric fuse of iron wire. No combustible material other than the iron wire was required to ignite the liquids. Combustible impurities and carbon dioxide were removed from the oxygen before admitting it to the bomb. Measurements of carbon dioxide and carbon monoxide formed in the combustion indicated that the liquids contained very little inert impurity, and that combustion was very nearly complete. The Washburn correction was applied to the results of the calorimetric measurements. The empirical equation

$$-\Delta H_{25}{}^{\circ}{}_{C}=259.28+648.84n+0.2587n^{2},$$

where $-\Delta H_{25}{}^{\circ}{}_{C}$ is the heat of combustion in international kilojoules per mole of liquid normal C_nH_{2n+2} in gaseous oxygen at 25° C and under a constant pressure of 1 atmosphere, the products of combustion being gaseous carbon dioxide and liquid water, also at 25° C, reproduces the mean values within 0.02 percent. The final experimental values are estimated to be accurate within 0.03 or 0.04 percent.

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I. INTRODUCTION

Accurate values of the heats of combustion of organic compounds are of importance in chemical thermodynamics chiefly because such values, together with data on the heats of formation of water and carbon dioxide, may be used to calculate the heats of formation of the compounds; and the heats of formation, together with the entropies of formation derived from specific heat and latent heat data in accordance with the third law of thermodynamics, may be used to calculate the free energies of formation of the compounds. For many organic compounds this is the only feasible method of obtaining the free energies of formation.

Accurate values for the heats of combustion of the gaseous normal paraffin hydrocarbons from methane to pentane have been reported by Rossini [14, 15].[1] Most previous data on the higher members of this series are not sufficiently accurate to permit the calculation of reliable free-energy values. For this reason, and because it is now possible to obtain materials of higher purity than those available to most previous investigators, it was desirable that new measurements of the heats of combustion of the normal paraffins above pentane be undertaken.

II. APPARATUS AND METHOD

The calorimeter and accessory apparatus, experimental procedure, and methods of calculating results have been described in detail previously [3,8].

The only feature of the methods of the present work which requires further description is the method of burning the samples of volatile liquids in the bomb. Samples of 0.5 to 1.0 g of liquid were inclosed in thin-walled glass bulbs which were flattened on opposite sides and filled completely with liquid in the manner described by Richards and Barry [13]. The flexible flat sides of the bulbs yielded sufficiently under the pressure (30 atmospheres) of the oxygen in the bomb, so that the pressure was supported by the inclosed liquid. The empty bulbs without the stems through which they were filled weighed from about 0.02 to 0.09 g each, the usual weight being about 0.03 to 0.04 g. The weights of the bulbs used by Richards and Barry varied from 0.3 to 0.5 g.

The samples were ignited by means of an electric fuse consisting of a 2-cm length of no. 36 AWG iron wire, which was wound in a small helix, attached to platinum leads about 0.2 mm in diameter, and placed in contact with the bulb containing the sample. It was not necessary to use any combustible material other than the iron wire to ignite the samples. The samples were burned in a cylindrical platinum crucible $\frac{5}{8}$ inch in height and $\frac{3}{4}$ inch in diameter.

The glass of the bulbs was fused during combustion, and after opening the bomb at the end of an experiment, was found in the form of one or more small globules on the bottom of the crucible. In some cases these globules were clear and in others they were darkened by some material distributed through the glass. This material was probably iron oxide, although there is a possibility that small amounts of unburned carbon may have been inclosed in the glass. The presence of carbon does not seem very probable, however, in view of the volatility of the liquids. The darkening of the glass globules did not appear to be associated with any systematic lowering of heat of combustion, or of the amount of carbon dioxide plus carbon monoxide formed in the combustion, and consequently if carbon was inclosed in the glass globules the amounts were probably negligible.

The thermal effect of solution of iron oxide and of gases in the molten glass was probably negligible.

The volume of the bomb used was 377 cm^3. One cubic centimeter of water was placed in the bomb before each experiment.

[1] Numbers in brackets refer to the literature references at the end of this paper.

III. MATERIAL

The samples of normal octane, nonane, decane, undecane, and dodecane used in this work were supplied by Prof. A. L. Henne of Ohio State University. They were prepared by Shepard, Henne, and Midgley [20] by distillation from petroleum. The normal heptane used was separated from petroleum at this Bureau by Hicks-Bruun and Bruun [5], and was further fractionally distilled by S. T. Schicktanz. The normal hexane was synthesized and purified by Mair [11].

The references cited contain data on the freezing points and boiling points of these compounds. These data indicate that the compounds were of a high degree of purity. Hick-Bruun and Bruun estimated the purity of the *n*-heptane to be better than 99 mole percent. Mair stated that the differences between the freezing points of the compounds synthesized by him and those separated from petroleum by Shepard, Henne, and Midgley indicate differences in purity of much less than 1 mole percent. The impurities most likely to be present in all the compounds are isomers, the heats of combustion of which probably do not differ from those of the normal compounds by more than a few tenths of 1 percent. The presence of 1 mole percent of isomers in a given normal compound would therefore affect the heat of combustion by only a few thousandths of 1 percent.

In the present work tests for inert impurities, such as dissolved water or air, were made by burning weighed samples of the liquids in the bomb under the same conditions as in the calorimetric measurements, and determining the amounts of carbon dioxide and carbon monoxide formed in the combustion. The carbon dioxide was determined by allowing the gaseous products of combustion to flow from the bomb through a drying tube containing Dehydrite ($Mg(ClO_4)_2 \cdot 3H_2O$) and P_2O_5, and then through a weighed glass-stoppered U-tube containing successively Ascarite (a sodium hydroxide-asbestos mixture) to absorb the CO_2, and Dehydrite and P_2O_5 to prevent loss of water vapor coming from the Ascarite. After the pressure in the bomb had been reduced to that of the atmosphere, hydrogen was admitted to the bomb to a pressure of about 10 atmospheres, and then released through the absorbing tubes mentioned above. This procedure was repeated several times until the residual mass of CO_2 in the bomb was negligibly small. The U-tube containing the Ascarite was then weighed and its increase in weight, corrected to vacuum, was taken as the mass of CO_2 formed in the combustion. The U-tube was filled with hydrogen in both the initial and final weighings, so that errors due to uncertainty in the value used for the change in volume of the Ascarite on absorption of CO_2 were negligible [14].

In the measurements on the normal paraffins from octane to dodecane, CO in the products of combustion was determined by C. Creitz of this Bureau, by the iodine pentoxide method described by Eiseman, Weaver, and Smith [4]. The amounts of CO found in the products of combustion of *n*-dodecane, *n*-undecane, *n*-decane, and *n*-octane were negligible. For *n*-nonane the carbon determined as CO amounted to 0.051 percent of the total carbon. Measurements of CO by the iodine pentoxide method were also made for one lot of *n*-heptane and for three measurements on *n*-hexane. The carbon determined

as CO by this method in the products of combustion of the *n*-heptane amounted to 0.064 percent of the total carbon, and the total carbon found was higher by about 0.06 percent than that calculated from the mass of *n*-heptane burned, on the assumption that it was pure. The carbon determined as CO in the products of combustion of the *n*-hexane amounted to about 2 percent of the total carbon, and the total carbon was higher by about 2 percent than that calculated from the mass of the samples burned. These data indicated that some trouble had developed in the iodine pentoxide apparatus, and as a result of this trouble the values obtained for CO in the products of combustion were too high. Hence, in the remaining measurements on *n*-hexane, CO was determined by another method. This method consisted in passing the products of combustion, after removal of the CO_2, through a copper tube heated to about 700° C, absorbing the CO_2 formed in Ascarite, and weighing it. These measurements gave for the carbon determined as CO, 0.032 percent of the total carbon. Tests by the iodine pentoxide method indicated no CO in the gas from the bomb after passing through the hot copper tube. Later another lot of *n*-heptane was obtained, and measurements of CO by the second method indicated that only 0.004 percent of the total carbon was present in the products of combustion as CO. The results on *n*-heptane reported in this paper are for this second sample.

Since nitric acid is formed from the nitrogen and water in the bomb, it is possible that some nitric acid may be carried out in the gaseous products of combustion, and be absorbed by the Ascarite. Calculations based on the partial pressure of nitric acid in the gas phase over aqueous solutions [6] indicate that the amount of nitric acid carried out in this manner is entirely negligible. In these calculations it was assumed that the gas in the bomb was at all times in equilibrium with that part of the solution which was condensed on the top and sides of the bomb where the concentration of nitric acid was greatest. The value for the concentration of the solution at these points was obtained in experiments in which the air initially in the bomb was not washed out prior to filling the bomb with oxygen, and consequently the total amount of nitric acid formed was about three times that normally formed.

In connection with the question as to whether nitric acid was carried out of the bomb in the gaseous products of combustion the following experiment was performed: A 1.5-g sample of benzoic acid was burned in the bomb, which had been filled with oxygen without washing out the air initially in it. The products of combustion were allowed to bubble slowly through about 10 cm^3 of distilled water in a glass U-tube which was filled with small glass beads and was immersed in an ice bath. After the pressure in the bomb had been reduced to 1 atmosphere, the bomb was filled several times with hydrogen to a pressure of about 10 atmospheres, and the hydrogen was allowed to bubble through the water in the U-tube. The total volume of gas bubbled through the water was about 40 liters. The water was then removed from the tube and titrated against a 0.01*N* solution of KOH, using phenolphthalein as an indicator. An approximately equal volume of distilled water was titrated against the same solution of KOH under the same conditions. No difference was detected between the distilled water and the water through which

the products of combustion had been bubbled. The method was sufficiently sensitive to detect about 0.1 mg of nitric acid in the water. Even if only one-third of the nitric acid vapor was absorbed in the water, the total mass of nitric acid vapor carried out of the bomb could hardly have exceeded 0.01 percent of the mass of carbon dioxide formed in the combustion.

The results of the measurements of carbon dioxide and carbon monoxide formed in combustion of the various compounds are summarized in table 1. In the third column of this table are given the ratios of the masses of carbon found to those calculated from the masses of the samples on the assumption that the compounds were pure. The values of atomic weights used in the calculations are C=12.009, H=1.0081, and O=16.000. All weights were corrected for the effect of the buoyancy of the air.

There is considerable evidence [2] that the values used for the atomic weights of carbon and hydrogen are more nearly correct than the present international values. The value 12.009 for carbon is believed to be accurate to ± 0.002, while the value 1.0081 for hydrogen is believed to be accurate to ± 0.0001.

It is very probably that organic liquids exposed to the air contain small amounts of inert impurities, such as dissolved air and water, and consequently it would be expected that the values $C_{found}/C_{calc.}$ given in table 1 would be slightly less than unity. This is seen to be the case for all the compounds listed in table 1 except *n*-nonane and *n*-dodecane. The high value of the carbon found for *n*-nonane is probably due to an error in the determination of CO by the iodine pentoxide method, which, as mentioned previously, gave too high results in some cases. If it were assumed that no CO was present in the products of combustion of this compound, the value of $C_{found}/C_{calc.}$ would be 0.999 68 instead of 1.000 19 as given in table 1, and the heat of combustion per gram of liquid would be lower by 0.021 percent than that given later, if no correction for unburned CO had been applied. Then if the departure from unity of the ratio $C_{found}/C_{calc.}$ were attributed to inert impurities and the value for heat of combustion corrected accordingly, the corrected value for heat of combustion of *n*-nonane would be higher by 0.011 percent than that given later. As some CO was probably present in the products of combustion, the error in the value given for the heat of combustion of *n*-nonane due to error in determining CO is probably less than 0.011 percent.

TABLE 1.—*Results of determinations of carbon dioxide and carbon monoxide in products of combustion of normal paraffin hydrocarbons*

Compound	Number of observations	$\frac{C_{found}}{C_{calc}}$	Deviation from mean	
			Average	Maximum
n-Hexane	5	0.999 89	±0.000 27	0.000 59
n-Heptane	5	.999 82	±.000 08	.000 13
n-Octane	5	.999 97	±.000 30	.000 70
n-Nonane	3	1.000 19	±.000 24	.000 36
n-Decane	3	.999 92	±.000 07	.000 10
n-Undecane	5	.999 97	±.000 13	.000 18
n-Dodecane	4	1.000 01	±.000 38	.000 76

It seems very unlikely that the high value of the carbon found for *n*-nonane could have been caused by the presence of higher members of the paraffin series as impurities, on account of the large amount of such impurities which would be required to explain the high value. For example, a mixture of nonane and decane containing 0.019 percent more carbon per gram than pure nonane would contain about 12 percent of decane.

The oxygen used was ordinary commercial oxygen, and contained some combustible impurities which were removed by passing the oxygen through a porcelain tube containing copper oxide heated to about 700° C. After this treatment the oxygen was passed through a tube containing Ascarite before being admitted to the bomb, in order to remove any CO_2 which might be present.

IV. CALIBRATION OF CALORIMETER

For the measurements on *n*-octane, *n*-nonane, *n*-decane, *n*-undecane, and *n*-dodecane, the energy equivalent, or effective heat capacity, of the calorimeter was the same as in the measurements on benzoic acid [8], namely, 13 587.$_2$ international joules per degree centigrade at 28.8° C, a value which was the result of a large number of electrical calibrations of the calorimeter.

Prior to the measurements on *n*-hexane a new resistance thermometer was constructed to replace the original thermometer which had not been entirely satisfactory, also some changes were made in the bomb which increased its heat capacity to some extent. It was therefore necessary to redetermine the energy equivalent of the calorimeter. This was done by burning 10 samples of "standard sample" benzoic acid in the calorimeter, using as the heat of combustion of this material the value recently determined at this Bureau [8], 26 414 international joules per gram mass when the charge is burned under the following standard conditions.

Temperature to which reaction is referred	30° C.
Initial oxygen pressure at 30° C	30 atm.
Mass of benzoic acid burned per unit of bomb volume	3 g/liter.
Mass of water placed in bomb per unit of bomb volume	3 g/liter.

The results of this calibration are given in table 2.

TABLE 2.—*Results of calibration of calorimeter for measurements on n-hexane*

Experiment	Observed energy equivalent at 30° C	Deviation from mean	
	*Int.*J/°C.	*Int.*J/°C.	*Percent*
1	13 601.4	+2.7	+0.020
2	13 592.6	−6.1	−.045
3	13 597.8	−0.9	−.007
4	13 594.4	−4.3	−.032
5	13 596.2	−2.5	−.018
6	13 596.5	−2.2	−.016
7	13 606.3	+7.6	+.056
8	13 601.7	+3.0	+.022
9	13 602.5	+3.8	+.028
10	13 597.2	−1.5	−.011
Mean	13 598.7	±3.5	±.025

After the measurements on *n*-hexane about a year elapsed before the measurements were made on *n*-heptane. During this time the gold washer in the bomb was replaced, the constants of the thermometer and the corrections to the bridge changed slightly, and a small amount of oil accumulated on the calorimeter heater. The calorimeter was therefore calibrated again by means of benzoic acid, immediately following the measurements on the *n*-heptane. The results of this calibration are shown in table 3.

TABLE 3.—*Results of calibration of calorimeter for measurements on n-heptane*

Experiment	Observed energy equivalent at 30° C	Deviation from mean	
	Int. j/°C	*Int.* j/°C	*Percent*
1	13 591.7	−3.6	−.026
2	13 591.3	−4.0	−.029
3	13 600.9	+5.6	+.041
4	13 594.9	−0.4	−.003
5	13 597.5	+2.2	+.016
Mean	13 595.$_8$	±3.2	±.026

The value of the energy equivalent calculated from the value given in table 2, the change in weight of the gold washer, and the weight of oil which accumulated on the calorimeter heater is 13 597$_6$ international joules per degree centigrade, a value which is 0.017 percent higher than the mean value given in table 3. The value given in table 3 was used in calculating the results of measurements on *n*-heptane.

V. RESULTS OF CALORIMETRIC COMBUSTION EXPERIMENTS

The results of the individual combustion experiments are given in table 4. Each observed value of heat of combustion under the conditions of the bomb process, $-\Delta U_B$, was reduced, by the method given by Washburn [23], to the difference, $-\Delta U_R$, in the internal energies of the initial system, consisting of liquid hydrocarbon and gaseous oxygen at 30° C and under a pressure of 1 atmosphere, and the final system, consisting of gaseous CO_2 and liquid water each separately at 30° C and under a pressure of 1 atmosphere. The reduction to $-\Delta U_R$ was made by Washburn's complete equation, modified so as to apply at 30° C instead of 20° C. The difference between $-\Delta U_B$ and $-\Delta U_R$ is less by about 20 percent at 30° than at 20° C.

The results are summarized in table 5. The observed values of $-\Delta U_R$ in column 2 were taken from table 4. The values of C_{found}/C_{calc} in column 3 were taken from table 1.

TABLE 4.—*Results of combustion experiments*

n-HEXANE

Experiment	Mass of sample (wt. in vacuo)	Initial oxygen pressure at 30° C	Final temperature of calorimeter	Observed heat of combustion	Reduction to $p=1$ atm	Reduction to 30° C	$-\Delta U_R$ at 30° C	Deviation from mean	
	g	atm	°C	*Int.* j/g	*Int.* j/g	*Int.* j/g	*Int.* j/g	*Int.* j/g	*Percent*
1	0.486 24	30.6	29.45	48 193.0	−7.7	−2.4	48 182.9	+12.3	+0.026
2	.687 42	31.3	30.00	48 171.6	−8.9	.0	48 162.7	−7.9	−.016
3	.704 48	30.5	29.84	48 183.1	−8.7	−.7	48 173.7	+3.1	+.006
4	.694 47	29.6	30.24	48 180.5	−8.6	+1.0	48 172.9	+2.3	+.005
5	.600 51	27.9	29.83	48 160.6	−7.6	−.7	48 152.3	−18.3	−.038
6	.569 63	29.5	30.30	48 185.5	−7.9	+1.3	48 178.9	+8.3	+.017
Mean							48 170.$_8$	±8.7	±.018

TABLE 4.—*Results of combustion experiments*—Continued

n-HEPTANE

Experiment	Mass of sample (wt. in vacuo)	Initial oxygen pressure at 30° C	Final temperature of calorimeter	Observed heat of combustion	Reduction to p=1 atm.	Reduction to 30° C	$-\Delta U_R$ at 30° C	Deviation from mean	
	g	atm	°C	*Int.* J/g	*Int.* J/g	*Int.* J/g	*Int.* J/g	*Int.* J/g	*Percent*
1	1.018 85	31.1	29.92	47 926.4	−11.2	−0.3	47 914.9	−6.3	−0.013
2	.921 18	30.7	29.38	47 948.4	−10.6	−2.0	47 935.8	+14.6	+.030
3	.896 79	30.6	30.01	47 935.6	−10.5	.0	47 925.1	+3.9	+.008
4	1.017 79	31.1	29.88	47 929.9	−11.1	−.4	47 918.4	−2.8	−.006
5	.903 58	30.5	30.28	47 909.8	−10.5	+.9	47 900.2	−21.0	−.044
6	1.011 96	30.9	30.29	47 943.3	−11.2	+.9	47 933.0	+11.8	+.025
Mean							47 921.2	±10.1	±.021

n-OCTANE

1	0.592 92	29.8	28.77	47 751.9	−8.8	−5.2	47 737.9	−6.8	−0.014
2	.546 31	30.1	29.77	47 738.2	−8.8	−1.0	47 728.4	−16.3	−.034
3	.493 43	29.8	30.04	47 750.6	−8.5	+.2	47 742.3	−2.4	−.005
4	.638 15	29.4	29.31	47 769.6	−9.1	−2.9	47 757.6	+12.9	+.027
5	.639 98	29.4	30.17	47 752.2	−9.2	+.7	47 743.7	−1.0	−.002
6	.543 23	29.1	29.68	47 768.2	−8.6	−1.3	47 758.3	+13.6	+.028
Mean							47 744.7	±8.8	±.019

n-NONANE

1	0.997 76	29.8	30.11	47 615.2	−11.4	+0.4	47 604.2	−1.7	−0.004
2	.967 18	29.8	30.16	47 604.4	−11.0	+.6	47 594.0	−11.9	−.025
3	.578 20	29.8	30.12	47 611.3	−9.0	+.5	47 602.8	−3.1	−.007
4	.655 62	30.1	29.93	47 597.4	−9.5	−.3	47 587.6	−18.3	−.038
5	.621 80	30.1	29.30	47 640.9	−9.5	−2.9	47 628.5	+22.6	+.047
6	.700 36	29.8	30.17	47 627.2	−9.5	+.7	47 618.4	+12.5	+.026
Mean							47 605.9	±11.7	±.025

n-DECANE

1	0.824 62	30.1	29.52	47 509.7	−10.4	−1.9	47 497.4	−0.9	−0.002
2	.820 19	30.1	30.09	47 508.1	−10.4	+.4	47 498.1	−.2	.000
3	.723 75	30.1	29.64	47 511.1	−9.5	−1.5	47 500.1	+1.8	+.004
4	.707 15	30.1	29.75	47 506.0	−10.0	−1.0	47 495.0	−3.3	−.007
5	.733 20	30.1	30.18	47 506.1	−10.0	+.7	47 496.8	−1.5	−.003
6	.789 18	30.1	30.26	47 511.5	−10.0	+1.1	47 502.6	+4.3	+.009
Mean							47 498.1	±2.0	±.004

n-UNDECANE

1	0.574 00	21.6	29.76	47 391.5	−7.6	−1.0	47 382.9	−18.9	−0.040
2	.850 56	28.8	29.81	47 408.1	−10.4	−.8	47 396.9	−4.9	−.010
3	.676 60	28.4	29.55	47 441.8	−9.5	−1.8	47 430.5	+28.7	+.061
4	.535 67	28.4	29.71	47 420.7	−9.0	−1.2	47 410.5	+8.7	+.018
5	.934 76	28.4	29.72	47 414.9	−10.9	−1.1	47 402.9	+1.1	+.002
6	.767 13	28.4	29.85	47 397.4	−9.9	−.6	47 386.9	+14.9	−.031
Mean							47 401.8	±12.9	±.027

n-DODECANE

1	0.483 37	29.8	29.91	47 348.4	−9.0	−0.4	47 339.0	−8.2	−0.017
2	.425 50	29.8	29.95	47 352.3	−8.5	−.2	47 343.6	−3.6	−.008
3	.576 51	29.1	29.84	47 359.7	−9.5	−.6	47 349.6	+2.4	+.005
4	.544 64	28.8	29.83	47 326.5	−9.0	−0.7	47 316.8	−30.4	−.064
5	.670 21	22.2	29.97	47 387.0	−8.0	−.1	47 378.9	+31.7	+.067
6	.429 34	21.6	30.06	47 362.3	−6.6	+.2	47 355.5	+8.3	+.018
Mean							47 347.3	±14.1	±.030

TABLE 5.—*Summary of results*

Substance	$-\Delta U_R$ observed at 30° C	$\frac{C_{found}}{C_{calc.}}$	$-\Delta U_R$ corrected at 30° C		$-\Delta H_{30°\,C}$ observed	$-\Delta H_{25°\,C}$		Obs.−Calc.
						Observed	Calculated	
	Int. j / g (*mass*)		*Int.* j / g	*Int.* kj / *mole*	*Int.* kj / *mole*	*Int.* kj / *mole*	*Int.* kj / *mole*	*Percent*
n-Hexane	48 170.6	0.999 89	48 175.9	4 151.19	4 160.1	4 161.8	4 161.6	−0.002
n-Heptane	47 921.2	.999 82	47 929.8	4 802.22	4 812.4	4 814.0	4 813.8	+.004
n-Octane	47 744.7	.999 97	47 746.1	5 453.46	5 464.8	5 466.6	5 466.6	+.000
n-Nonane	47 605.9	1.000 19	47 605.9	6 105.12	6 117.8	6 119.8	6 119.8	+.000
n-Decane	47 498.3	.999 92	47 502.1	6 758.04	6 772.0	6 774.2	6 773.8	+.010
n-Undecane	47 401.8	.999 97	47 403.2	7 408.82	7 424.0	7 426.4	7 427.8	−.019
n-Dodecane	47 347.2	1.000 01	47 347.2	8 064.04	8 080.8	8 083.2	8 082.8	+.007

The corrected values of $-\Delta U_R$ in column 4 were obtained from the observed values on the assumption that the departures from unity of the ratios $C_{found}/C_{calc.}$, where these ratios are less than unity, are due to inert impurities. The conversion to international kilojoules per mole was made using the atomic weights C=12.009 and H=1.0081. This method of calculation is equivalent to determining the mass of hydrocarbon burned from the mass of CO_2 formed in the complete combustion of the sample. Hence an error of 0.001 in the value used for the atomic weight of carbon would cause an error of only 1 in 44 000 in the heat of combustion per mole of hydrocarbon. Where the observed ratio $C_{found}/C_{calc.}$ is greater than unity, as in the case of *n*-nonane, an error of 0.001 in the atomic weight of carbon would cause an error of about 0.007 percent in the heat of combustion per mole of hydrocarbon.

The observed values of $-\Delta H_{30°\,C}$ for the reaction:

$$C_nH_{2n+2}(liq)+\frac{3n+1}{2}O_2(gas)$$
$$=nCO_2(gas)+(n+1)H_2O(liq)\ (30°\ C, p=1\ atm)$$

which are given in column 6 of table 5 were obtained by adding to the values of $-\Delta U_R$ in column 5 the values of $-\Delta(pV)$ for the above reaction. The reduction to 25° C was made using the specific heat data taken from International Critical Tables [7]. These data are given in table 6.

TABLE 6.—*Specific heat data used in calculating temperature coefficients of heats of combustion*

Substance	C_p (p=1 atm)	Temperature	Substance	C_p (p=1 atm)	Temperature
	j/*mole* °C	°C		j/*mole* °C	°C
Oxygen (gas)	29.18	28	n-Octane (liquid)	241.3	0 to 50
Carbon dioxide (gas)	36.90	28	Nonane (liquid)	269.9	0 to 50
Water (liquid)	75.23	28	Decane (liquid)	298.9	0 to 50
n-Hexane (liquid)	190.0	0 to 50	Undecane (liquid)	327.7	0 to 50
n-Heptane (liquid)	212.6	0 to 50	Dodecane (liquid)	356.5	0 to 50

The values of $-\Delta H_{25°\,C}$ in column 8 of table 5 were calculated by means of the following empirical equation, which was derived by the method of least squares:

$$-\Delta H_{25°\,C}=259.28+648.84n+0.2587n^2,$$

where n is the number of carbon atoms per molecule. As shown in the last column of table 5 the average difference between observed

and calculated results is about 0.01 percent, and the maximum difference about 0.02 percent. This agreement is somewhat better than would be expected from the precision of the various measurements, and may be partly fortuitous. It is believed, however, that the experimental results are accurate within about 0.03 to 0.04 percent.

If $n=5$ is substituted in the preceding equation, the calculated value 3 509.95 international kilojoules per mole is obtained for the heat of combustion of liquid *n*-pentane at 25° C and a constant pressure of 1 atmosphere. Rossini [15] has reported the value 3 536.00 ±0.88 international kilojoules per mole for the heat of combustion of gaseous *n*-pentane at 25° C and at constant pressure, and from a review of existing data [16] has selected 6.3 kilocalories per mole, or 26.35 international kilojoules per mole, as the most probable value for the heat of vaporization of *n*-pentane at 25° C. Subtracting this value for heat of vaporization from Rossini's value for the heat of combustion of gaseous *n*-pentane gives 3 509.65 international kilojoules per mole for the heat of combustion of liquid *n*-pentane, a value which is in agreement within 0.01 percent with that obtained by extrapolation of the data of the present work.

Values obtained by substituting 2, 3, and 4 for n in the preceding equation are higher, by amounts greater than the experimental uncertainties, than the heats of combustion of liquid ethane, propane, and normal butane, respectively, obtained by combining Rossini's data on heats of combustion of gaseous ethane, propane, and normal butane with values for the heats of vaporization of these compounds. This is to be expected, for Rossini has shown [17] that although there is a linear relation between heat of combustion and the number of carbon atoms in the molecule for the gaseous normal paraffin hydrocarbons above *n*-pentane, this relation does not hold for the gaseous normal paraffins below *n*-pentane.

VI. PREVIOUS WORK

Values of the heats of combustion of liquid normal paraffin hydrocarbons deduced from data reported by previous investigators are compared in table 7 with the results of the present work.

TABLE 7.—*Results deduced from data of previous investigators compared with results of present work*

[Values of $-\Delta U_n$ at 30° C are given in international joules per gram mass. Figures in parentheses represent percentage differences from results of present work.]

Investigator	*n*-Hexane	*n*-Heptane	*n*-Octane	*n*-Decane	*n*-Dodecane
Louguinine	----------	[a] 47 360 (−1.2)	----------	----------	----------
Stohmann, Kleber, and Langbein	[b] 47 909 (−0.43)	----------	----------	----------	----------
Zubow	[a] [c] 47 934 (−0.50)	----------	[a] [c] 47 599 (−0.31)	[a] [c] 47 267 (−0.50)	----------
Richards and Jesse	----------	----------	47 542 (−0.43)	----------	----------
Jessup (unpublished)	----------	[b] 47 894 (−0.075)	[b] 47 712 (−0.071)	----------	----------
Roth	----------	----------	[a] 47 777 (+0.065)	----------	----------
Banse and Parks	----------	----------	[a] 47 761 (+0.031)	----------	[a] 47 349 (+0.004)
Present work	48 176	47 930	47 746	47 502	47 347

[a] Experimental conditions not given in sufficient detail to permit comparison with present work to be made with certainty.
[b] Results are probably too low on account of loss of liquid by evaporation.
[c] The Washburn correction has not been applied to these values.

Measurements of the heat of combustion of liquid *n*-hexane by means of a bomb calorimeter were made by Zubow [24], and by Stohmann, Kleber, and Langbein [21]. Zubow reported the value 11 602.6 calories per gram weighed in air for the heat of combustion at 18° C under the conditions of the bomb process. He also reported the value 9706 calories per gram weighed in air for the heat of combustion of naphthalene under the same conditions. Using the value 1.5203, based on Dickinson's [3] work, for the ratio of the heats of combustion per gram in air of naphthalene and benzoic acid at about 25° C, and the value reported by Jessup and Green [8] for the heat of combustion of benzoic acid at 25° C and under the standard conditions mentioned previously, 26 440 international joules per gram weighed in air, the heat of combustion of naphthalene at 25° C and under the conditions of the bomb process is calculated to be 40 197 international joules per gram weighed in air. Upon reduction to 18° C the heat of combustion of naphthalene becomes 40 207 international joules per gram weighed in air. Multiplying Zubow's value for *n*-hexane by the ratio 40 207/9 706, reducing to 30° C and correcting for air buoyancy, there is obtained the value 47 934 international joules per gram mass for the heat of combustion under the conditions of the bomb process. Application of the Washburn correction probably would not change the value given above by more than about 0.03 percent.

Stohmann, Kleber, and Langbein [21] made two measurements of the heat of combustion of liquid *n*-hexane at about 15° C and under an initial oxygen pressure of 24 atmospheres. The volume of their bomb was 294 cm^3. Combustible impurities were removed from the oxygen by passing it through a red-hot copper tube. No water was placed in the bomb, but the oxygen was not dried before compressing it, and presumably was saturated with water vapor. In the first experiment the platinum crucible was covered with a thin sheet of collodion to prevent evaporation of the *n*-hexane. In the second experiment the sample was burned in a glass bulb having two necks, one of which was very narrow. The larger neck was closed by a drop of molten stearic acid, and the *n*-hexane was introduced through the smaller neck. It appears doubtful whether either of these devices entirely prevented evaporation. The two results agreed within 0.06 percent, the mean being 11 501.2 calories per gram (in air?) under the conditions of the bomb process. Stohmann, Kleber, and Langbein also measured the heat of combustion of benzoic acid [22] under the conditions mentioned above, and obtained the value 6322.3 calories per gram (weighed in air?). After application of the Washburn correction, reduction to 30° C, correction for air buoyancy, and reduction to present energy units on the basis of data on the heat of combustion of benzoic acid by Stohmann, Kleber, and Langbein, and by Jessup and Green [8], the data on *n*-hexane by Stohmann, Kleber, and Langbein yield the value 47 969 international joules per gram mass for $-\Delta U_B$ at 30° C.

Louguinine [10] reported the value 1 137 450 calories per mole for the heat of combustion of liquid *n*-heptane. The measurement was made at constant pressure, and the mass of sample burned was calculated from the mass of carbon dioxide formed in combustion. The temperature to which the reaction is referred, and the atomic weights of carbon and oxygen are not given, and the relation of the energy

unit used to the present units is not known. Using the relation, 1 calorie=4.1833 international joules, Louguinine's value for *n*-heptane becomes 4 758 international kilojoules per mole. The corresponding value of $-\Delta U_R$ is 47 360 international joules per gram.

The present writer in 1927 made two measurements of the heat of combustion of *n*-heptane and two measurements of the heat of combustion of *n*-octane. The data were not published but the values obtained were given by Kharasch [9] in a review of the literature on heats of combustion of organic compounds. The samples were burned in gelatin capsules, which did not entirely prevent loss of liquid by evaporation. The calorimeter was calibrated with benzoic acid. The two results on *n*-heptane agreed within 0.08 percent, while the two results on *n*-octane agreed with 0.02 percent. The mean values of $-\Delta U_R$ at 30° were, expressed in international joules per gram mass, 47 894 for *n*-heptane, and 47 712 for *n*-octane.

Richards and Jesse [12] reported the results of two measurements of the heat of combustion of *n*-octane. They give their results in terms of the temperature rise of their calorimeter produced by burning together in the bomb, a known mass of *n*-octane and a known mass of sucrose. They also give the temperature rise produced by the combustion of a known mass of sucrose alone in the bomb. The present writer has applied the Washburn correction and recalculated their results, using the value 1.6027, based on Dickinson's [3] work, for the ratio of the heats of combustion per gram weighed in air of benzoic acid and sucrose, at about 25° C and under an initial oxygen pressure of 30 atmospheres, and the value 26 440 international joules per gram [8] (weighed in air) for the heat of combustion of benzoic acid at 25° C and under the standard conditions mentioned previously. The two recalculated values for the heat of combustion of *n*-octane agree within 0.04 percent, the mean value of $-\Delta U_R$ being 47 542 international joules per gram mass.

Zubow [24] reported the value 11 519.9 calories per gram weighed in air for the heat of combustion of *n*-octane. After recalculation in the manner described for *n*-hexane this value becomes 47 599 international joules per gram mass.

Roth [18] determined the heat of combustion of *n*-octane by means of a bomb calorimeter. The data were not published, but the value 11 449 calories per gram weighed in air is given in the Landolt-Börnstein tables. As the conditions under which this value was obtained and the energy unit used are not known, comparison with the results of the present work cannot be made with certainty. Assuming that the temperature to which the combustion was referred was 20° C, the initial oxygen pressure 35 atmospheres, and the calorie used was equal to 4.184 international joules, the value of $-\Delta U_R$ at 30° C calculated from Roth's value given above is 47 777 international joules per gram mass.

Zubow [24] reported the value 11 438.8 calories per gram weighed in air for the heat of combustion of liquid *n*-decane at 18° C and under the conditions of the bomb process. This value when recalculated in the manner described for *n*-hexane and *n*-octane becomes 47 267 international joules per gram mass.

Banse and Parks [1] in Roth's laboratory made three measurements of the heat of combustion of *n*-octane and four measurements of the heat of combustion of *n*-dodecane. The samples used were prepared by

Shepard, Henne, and Midgley [20], and were therefore probably identical with the samples of *n*-octane and *n*-dodecane used in the present work. The measurements were made at 19° C by means of a bomb calorimeter which was standardized with benzoic acid, using the value 6 324 calories per gram weighed in air for the heat of combustion of this substance. The average deviation from the mean of the individual results was 0.10 percent for *n*-octane, and 0.08 percent for *n*-dodecane. The values reported for the heats of combustion under the conditions of the bomb process are 11 434 calories per gram mass for *n*-octane, and 11 335 calories per gram mass for *n*-dodecane. After reduction to the present energy units, using data on the heat of combustion of benzoic acid by Jessup and Green [8], application of the approximate Washburn correction, and reduction to 30° C, the data of Banse and Parks yield for $-\Delta U_R$ the values 47 761 international joules per gram mass for *n*-octane and 47 349 international joules per gram mass for *n*-dodecane. There is some uncertainty in the application of the Washburn correction to the data of Banse and Parks, as they do not give the volume of their bomb, the mass of the samples burned, or the mass of water placed in the bomb. They refer to Roth's Thermochemie for details of the procedure. On page 78 of this work Roth states that usually 5 cm^3 and occasionally 10 cm^3 of water was placed in the bomb. The approximate Washburn correction which was applied in obtaining the values of $-\Delta U_R$ given above from the data of Banse and Parks was based on the assumption that the bomb volume was ⅓ liter, and the masses of water and sample of combustible were each 3 g per liter of bomb volume. The effect of using a larger amount of water would be partially compensated for if the same mass of water was used in the calibration of the calorimeter with benzoic acid. Assuming the volume of the bomb to be ⅓ liter, and the mass of the samples of benzoic acid to be 1 g, the effect of the heat of solution of carbon dioxide in the water is greater by 0.04 percent of the heat evolved with 5 cm^3 of water in the bomb, than with 1 cm^3. For the hydrocarbons the difference amounts to about 0.03 percent, assuming 1-g samples. Hence, if 5 cm^3 of water was placed in the bomb by Banse and Parks, the values of $-\Delta U_R$ calculated from their data may be too low by about 0.01 percent. The error may not be quite as large as this, however, on account of the fact that with such a large quantity of water in the bomb, the water may not be entirely saturated with carbon dioxide at the end of an experiment. Roth [19] has determined the heat capacity of his calorimeter by means of benzoic acid with 1, 5, and 10 g of water in the bomb, without applying the Washburn correction. The values obtained with 5 and 10 g of water in the bomb were lower by 0.011 and 0.064 percent, respectively, than the value obtained with 1 g of water in the bomb. The corresponding differences calculated by the method given by Washburn [23] are 0.046 and 0.102 percent, respectively. The actually observed effect of the larger amount of water is therefore of the order of half the calculated effect.

No data on the heats of combustion of *n*-nonane and *n*-undecane have been found in the literature.

The author is indebted to C. B. Green for making the calorimetric measurements on *n*-dodecane.

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RESEARCH PAPER RP967

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SEPARATION OF CONSTANT-BOILING MIXTURES OF NAPHTHENE AND PARAFFIN HYDROCARBONS BY DISTILLATION WITH ACETIC ACID.[1]

By Sylvester T. Schicktanz [2]

ABSTRACT

Constant-boiling fractions of gasoline normally boiling in the temperature range 130 to 174° C, and consisting of naphthene and paraffin hydrocarbons, have been successfully separated by distilling with acetic acid. The azeotropic mixtures formed by the hydrocarbons and the acid aid in separately concentrating the paraffin and naphthene groups, which, although never absolutely pure, can be separated further by other physical methods.

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I. INTRODUCTION

It is very difficult and sometimes impossible to obtain pure hydrocarbons from gasoline by fractional distillation alone. This is especially true of gasoline consisting of varying amounts of the two types of hydrocarbons, naphthenes, and paraffins, which are distributed throughout the boiling range. This is caused in part by the tendency of the different types of hydrocarbon molecules present to form azeotropic mixtures, and in part by the fact that the boiling points of the different substances are so close together that separation by distillation is impractical.

Although the various homologous series of hydrocarbons belong to the class of substances known as molecularly nonassociated,[3] their mixtures deviate considerably from the laws of ideal solutions. This is shown by the work of previous investigators [4, 5] who have studied the simple binary mixture of benzene and *n*-hexane, which cannot be

[1] Financial assistance for this work has been received from the research fund of the American Petroleum Institute. This work is part of Project 6, The Separation, Identification, and Determination of the Constituents of Petroleum.

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separated quantitatively by systematic fractional distillation alone. Such systems, which deviate considerably from Raoult's law of solutions, may be successfully separated by distillation if a third component [6] is added. Under these conditions, the equilibrium is altered by the formation of new azeotropic mixtures. The effectiveness of such a separation will depend, however, upon the difference in molecular structure of the various hydrocarbons in question,[7] and the characteristics of the third component. It is essential, also, that the added component shall not react with, or polymerize, the hydrocarbons, and shall be readily and quantitatively removable from the hydrocarbons after the separation has been effected.

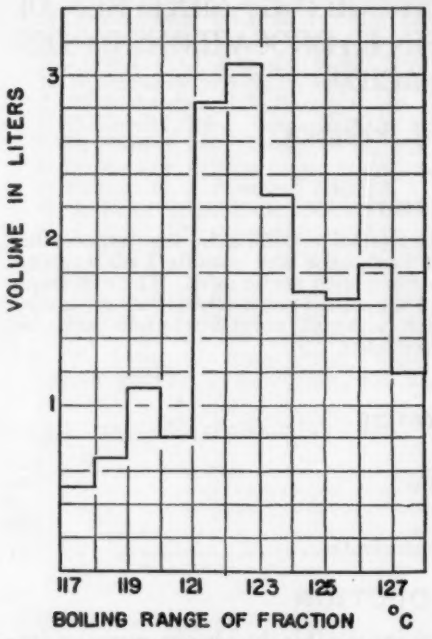

FIGURE 1.—*Distribution of the petroleum distillate by volume with respect to boiling range at 215-*mm *pressure*

Glacial acetic acid, which is highly molecularly associated,[8] has been found in this laboratory to be very effective as a third component in the separation of constant-boiling fractions of gasoline consisting of naphthene and paraffin hydrocarbons. Although acetic acid is a low-boiling liquid (118.1° C), it tends to form azeotropes with hydrocarbons boiling over a considerable temperature range, and can be used successfully for the separation of the constant-boiling fractions of gasoline normally boiling in the range 130 to 174° C. It is also inexpensive, does not attack or decompose the hydrocarbons in question, and is readily removed quantitatively from the hydro-carbons by washing with water.

II. DESCRIPTION OF THE FRACTION OF GASOLINE

The gasoline fraction, consisting essentially of naphthene and paraffin hydrocarbons, was obtained by removing the aromatic hydrocarbons from a carefully fractionated portion of petroleum, boiling between 118 and 130° C at 215-mm pressure,[9] which corresponds to 162 to 174° C at 760 mm. The bulk of the aromatic hydrocarbons was removed first by extraction with liquid sulphur dioxide [10] at −35° C. The hydrocarbons immiscible with sulphur dioxide were subsequently treated with concentrated sulphuric acid for 22 hours at room temperature to remove all the remaining aromatic substances. The

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remaining unsulphonated oil layer, consisting essentially of naphthene and paraffin hydrocarbons, was washed repeatedly with sodium carbonate and then with water in order to remove all traces of sulphuric acid or sulphonated products. This mixture of hydrocarbons was then subjected to a systematic distillation at 215-mm pressure in a column packed with locket-chain.[11]

Little separation was produced by the third systematic distillation. In table 1 are shown the results of a third systematic distillation of one of the portions of oil, which consisted of a number of fractions from the second distillation combined according to boiling point and refractive index. The spread of the boiling points and refractive indices of the distilled fractions is almost identical with the spread of the boiling points and refractive indices of the fractions used to make up the original charge. The total amount of material of the original isodecane fraction was apparently so well distributed over its temperature range by the third systematic distillation that further fractionation by straight distillation of the oil appeared to be impractical. The distribution by volume of the isodecane fraction with respect to boiling-point range is shown in figure 1.

TABLE 1.—*Separation obtained during the third systematic fractionation of the gasoline*

Fraction	Percentage of charge distilled	Boiling point at 215 mm Hg	Refractive index n_D^{25}
Original		122 to 123	1.4221 to 1.4268
1	4.07	122.2	1.4259
2	3.82	122.3	1.4249
3	3.62	122.3	1.4249
4	3.82	122.4	1.4249
5	3.95	122.4	1.4252
6	3.36	122.4	1.4253
7	3.36	122.3	1.4248
8	3.69	122.3	1.4246
9	3.36	122.3	1.4246
10	4.26	122.3	1.4234
11	2.13	122.3	1.4239
12	3.56	122.3	1.4245
13	4.07	122.4	1.4238
14	3.17	122.4	1.4234
15	3.36	122.4	1.4236
16	3.88	122.4	1.4234
17	3.62	122.4	1.4230
18	3.36	122.6	1.4228
19	3.24	122.7	1.4229
20	3.24	122.7	1.4226
21	3.82	122.7	1.4230
22	3.24	122.9	1.4225
23	3.69	123.0	1.4226
24	3.88	123.0	1.4214
25	3.43	123.2	1.4214
26	3.88	123.2	1.4213
27	3.43	123.3	1.4212
28	3.62	123.4	1.4213

According to the refractive indices, each 1.0° C fraction, throughout the distillation range, consisted of a mixture of varying amounts of naphthene and paraffin hydrocarbons, with no indication of the separation of a pure hydrocarbon.

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III. METHOD

Each of the 1° fractions could be separated further by distillation upon the addition of acetic acid (glacial) to the oil. An excess of acid was used at all times in order to have pure acetic acid remaining in the still pot after all the hydrocarbons had been removed. This made it possible to distill the oil at temperatures below the boiling point of acetic acid (118.1° C), thereby decreasing the possibility of changing the composition of the oil by cracking or polymerization. This required approximately a 4:1 ratio of acid to oil, since the azeo-

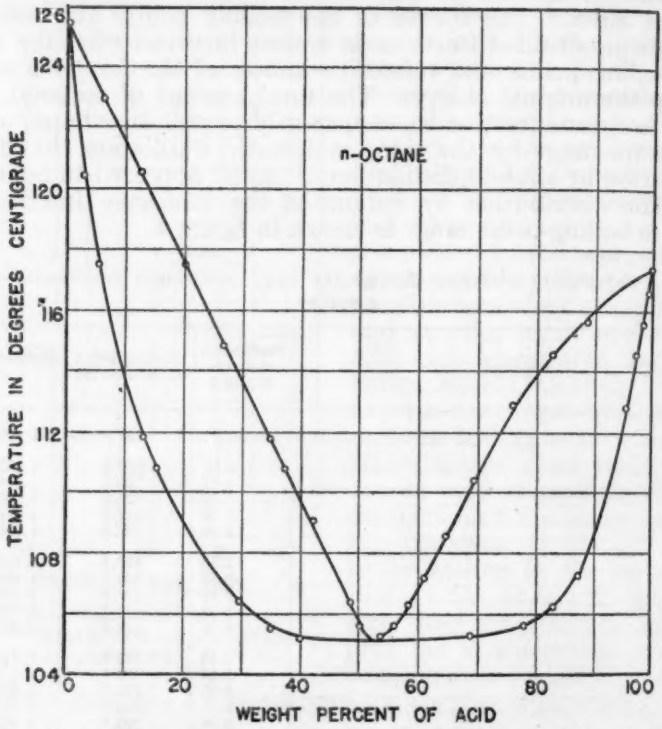

FIGURE 2.—*Composition-temperature diagram for the vapor and liquid phases for the binary mixture of n-octane and acetic acid.*

tropes formed by the hydrocarbons of the oil fraction having a boiling point of 123° C at 215-mm pressure contained between 70 and 77 percent of acid.

Because of this procedure only that part of the system which consisted of the azeotropes and acetic acid was made use of in the distillation. This is illustrated in figure 2, which shows the composition-temperature diagram of both the vapor and liquid phases for the binary system of *n*-octane and acetic acid. The minimum boiling point of this binary system is 105.1° C at 760-mm pressure and consists of 52.5 percent by weight of acid and 47.5 percent of hydrocarbon. The boiling point and the percentage of acid in the azeotrope increase as the number of carbon atoms in the hydrocarbon molecule is increased. For example, a gasoline fraction boiling at 132° C at 760-mm pressure formed an azeotrope consisting of approximately 56 percent by weight of acid.

The azeotropic mixtures of acid and hydrocarbons were distilled into 100-ml fractions at a rate of approximately 1 ml per minute at atmospheric pressure. The separation of the hydrocarbons occurring during the distillation was followed by determining the refractive index of the oil in every second or every fifth fraction. The acetic acid was removed from the oil of each fraction by washing three times with water in a separatory funnel before determining the refractive index. Although the acid distillations afforded an effective separation of the two classes of hydrocarbons in the constant-boiling fractions of gasoline, it was necessary to subject the intermediate cuts to several successive acid distillations in order to concentrate the bulk of the paraffins and naphthenes into separate fractions, leaving only a small amount of material which was intermediate in composition. Because of the corrosive action of the acetic acid, it was not possible to use the chain-packed columns and, consequently, all the separations were made in an all-glass 30-bubble-cap column.[12]

IV. RESULTS

In table 2 are given the results of a distillation, which is characteristic of all the distillations carried out. The first portion of distillate invariably separated into two layers, presumably because of the water in the acetic acid. In many instances, the hydrocarbons recovered from this first fraction had a high refractive index, indicating inefficiency of separation caused by the formation of a complex azeotropic system consisting of acid, water, and hydrocarbons. The remaining fractions obtained during these distillations were homogeneous at room temperature, and the refractive index, beginning low, gradually increased.

TABLE 2.—*Acid distillation of a constant-boiling fraction of gasoline n_D^{25} 1.4225 to 1.4238; bp_{215} 122 to 123°C*

Fraction	Volume of fraction, acid plus oil	Refractive index of acid-free oil of specified cuts n_D^{25}	Fraction	Volume of fraction, acid plus oil	Refractive index of acid-free oil of specified cuts n_D^{25}
	ml			ml	
Original	500 oil 1,500 acetic acid		11	104	
1	100	1.4132	12	104	
2	117		13	104	
3	113		14	101	
4	110		15	102	1.4251
5	109	1.4142	16	114	
6	105		17	106	
7	119		18	105	
8	112		19	68	1.4400
9	102				
10	111	1.4174			

In the constant-boiling fractions of gasoline, the paraffin hydrocarbons, which produce the most abnormal solutions with acetic acid, form azeotropic mixtures which are lower-boiling than those formed by the naphthenes. This is clearly shown in column 3 of table 2. The first substance removed from the complex mixture of the originally charged oil by the distillation has a low refractive index which ap-

[12] J. H. Bruun and S. T. Schicktanz, BS J. Research 7, 851 (1931) RP370.

proaches that of the paraffin hydrocarbons. As the distillation proceeds, the refractive index of the fractions increases and approaches that of the naphthene hydrocarbons.

Although the acid distillation concentrates the paraffin hydrocarbons in the fore part of the distillation and the naphthenes in the latter part, neither group of hydrocarbons can be obtained in a pure state. It appears that the azeotropes formed are not truly simple binary mixtures, but are either ternary mixtures consisting of a large percentage of one type of hydrocarbon, a small amount of the other, and acetic acid, or complex mixtures of binary azeotropes having a constant boiling point. This is substantiated by the ineffective separation produced by redistilling a charge of material of low refractive index. In table 3 are given the results of such a distillation. Very little separation occurred, as is seen by the large volume of material of constant refractive index occurring during the fore part of the distillation.

TABLE 3.—*Redistillation of material of low refractive index*

Fraction	Volume of fraction, acid and oil	Refractive index of acid-free oil n_D^{25}	Fraction	Volume of fraction, acid and oil	Refractive index of acid-free oil n_D^{25}
	ml			ml	
Original material		1.4160 to 1.4210	11	101	
			12	106	
1	93	1.4172	13	104	
2	101		14	114	
3	106		15	96	1.4172
4	100				
5	108	1.4172	16	102	
			17	113	
6	102		18	141	1.4183
7	107		19	106	
8	124		20	110	1.4267
9	110				
10	114	1.4172	21	104	

V. FURTHER SEPARATION OF ACETIC ACID CONCENTRATES

The material with a constant refractive index, which can not be separated further by acid distillation, can be further resolved by subjecting the oil, free from acid, to a simple fractional distillation. In table 4 are shown the results obtained by distilling such a concentrate at 215-mm pressure. The paraffins concentrated apparently in the latter part of the distillation, as is evidenced by the fractions of low refractive index, shown in column 4 of the table. The material in the fore part of the distillation, with an index higher than that of the starting material, can be further separated by an acid distillation.

The curves in figure 3 summarize the relative effectiveness of the various types of distillation. Curve 1 shows the separation occurring during the third systematic distillation of the oil, at 215-mm pressure, using an efficient locket chain packed column. Curve 3 shows the separation obtained during the first acid distillation of a narrow-boiling fraction of gasoline. Curve 2 shows the ineffectiveness of the acid treatment when dealing with a previously distilled paraffin concentrate and curve 4 shows the separation obtained by distilling an acid-free paraffin concentrate at 215-mm pressure.

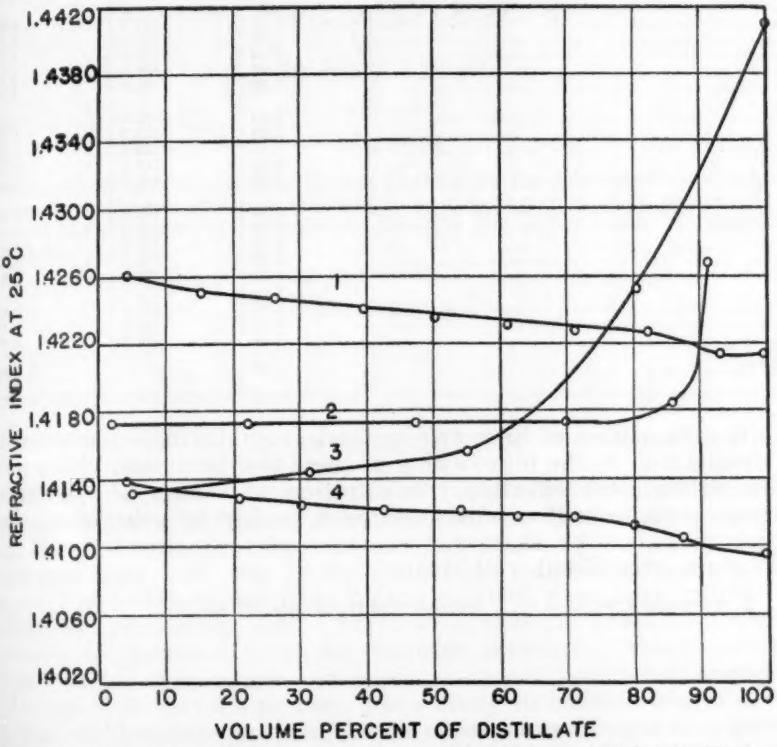

FIGURE 3.—*Separation obtained in the various distillations: (1) Oil distillation at 215-mm pressure; (2) acetic acid redistillation of a low refractive index concentrate; (3) acetic acid distillation of a constant-boiling fraction of gasoline; (4) oil distillation at 215-mm pressure of a paraffin fraction previously concentrated by acetic acid distillation.*

TABLE 4.—*Distillation at a pressure of 215* mm Hg *of the concentrate of low refractive index from acetic acid distillation*

Fraction	Percentage of charge distilled	Boiling point at 215 mm Hg	Refractive index n_D^{25}
Original			1.4114 to 1.4120
1	4.14	121.4	1.4138
2	4.91	121.8	1.4138
3	3.99	121.8	1.4129
4	3.99	121.9	1.4128
5	4.14	121.9	1.4128
6	3.39	121.9	1.4126
7	3.32	122.0	1.4125
8	2.32	122.0	1.4124
9	2.65	122.0	1.4123
10	2.82	122.0	1.4123
11	3.49	122.0	1.4122
12	3.65	122.1	1.4121
13	3.81	122.1	1.4120
14	3.99	122.1	1.4120
15	3.32	122.1	1.4121
16	5.00	122.1	1.4119
17	3.49	122.2	1.4117
18	3.65	122.3	1.4117
19	5.00	122.5	1.4117
20	4.31	122.6	1.4116
21	4.31	122.6	1.4113
22	3.81	122.6	1.4109
23	4.14	122.6	1.4104
Residue	12.46		1.4095

Although neither of these two methods, acid distillation or straight oil distillation, or the interlocking of these two processes, yields pure hydrocarbons, the effective concentration of each type of hydrocarbons permits further separation more readily by other methods.[13]

WASHINGTON, October 21, 1936.

[13] J. D. White and F. W. Rese, Jr., J. Research NBS 17, 943 (1936) RP955.

U. S. DEPARTMENT OF COMMERCE NATIONAL BUREAU OF STANDARDS

RESEARCH PAPER RP968

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DETERMINATION OF SULPHUR OCCURRING AS SULPHIDE IN PORTLAND CEMENT

By Harry A. Bright

ABSTRACT

A modification of the usual evolution method for the determination of sulphur is described wherein stannous chloride is used during solution of the sample to prevent the oxidation of hydrogen sulphide by the higher oxides of manganese and iron.

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I. INTRODUCTION

Among the minor constituents of certain portland cements are small amounts of sulphides associated with compounds of manganese and iron. The manganese is usually in valence states higher than 2 and interferes with any determination of sulphides based on the amount of hydrogen sulphide that is evolved when a sample is dissolved in hydrochloric acid. Ferric iron, which is practically always present in portland cements, likewise interferes. Sulphides and higher oxides of manganese in portland cement may seem incompatible, but both may be present, particularly in blended cements.

Watson [1] has recommended the use of stannous chloride to overcome the effect of ferric iron. Stannous chloride for this purpose was independently used at this Bureau in connection with an investigation on the reducing and oxidizing constituents of cements. As will be shown later, it was found that the addition of this salt also prevented interference by higher oxides of manganese. Titanous chloride and zinc dust were not as efficient as stannous chloride. The procedure developed at this Bureau is given in section II.

II. PROCEDURE

Transfer 5 g of the sample to a *dry* 500-ml flask and connect the latter as shown in figure 1. Place 15 ml of an ammoniacal solution of zinc sulphate and 285 ml of distilled water in the tall-form beaker.[2]

[1] Cement 5, 49 (1932).

[2] For very small amounts of sulphides, an ammoniacal solution of $CdCl_2$ can be substituted, as the yellow CdS facilitates detection of traces of sulphides.

Add 10 ml of water through the thistle tube, and shake the flask to wet the cement completely. Add 25 ml of stannous chloride solution, shake several times to mix, and then add 65 ml of diluted hydrochloric acid (10+3). Connect the inlet tube, pass a *slow* stream of air [3] through the system, and heat the flask and contents slowly until boiling ensues. Boil gently for 5 to 6 minutes, cut off the heat and continue the passage of air for 3 to 4 minutes. Disconnect the delivery tube, and leave it in the solution for use as a stirrer.[4] Add 2 ml of starch solution and then 40 ml of diluted hydrochloric acid (1+1). Titrate immediately with the iodate solution until a permanent blue color is obtained. Subtract the blank obtained with the reagents alone, and calculate the percentage of sulphur.

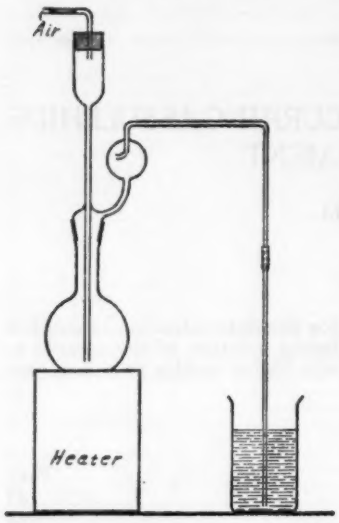

FIGURE 1.—*Apparatus for the determination of sulphide sulphur.*

Ammoniacal zinc sulphate.—Dissolve 50 g of $ZnSO_4.7H_2O$ in 150 ml of water and 350 ml of NH_4OH (sp gr 0.90). Let stand 24 hours and filter.

Stannous chloride.—To 10 g of $SnCl_2.2H_2O$, in a small flask, add 7 ml of diluted HCl (1+1). Warm gently until the salt is dissolved. Cool, and add 95 ml of water. This reagent should be made up daily as needed, as the salt tends to hydrolyze.

Starch solution.—To 500 ml of boiling distilled water, add a cold suspension of 5 g of soluble starch in 25 ml of distilled water, cool, add a cool solution of 5 g of NaOH in 50 ml of distilled water, then add 15 g of KI, and mix thoroughly.

Potassium iodate.—(0.03*N*) Dissolve 1.12 g of KIO_3 and 12 g of KI in 1,000 ml of distilled water. Standardize by means of sodium oxalate through $KMnO_4$ and $Na_2S_2O_3$ as follows: To 300 ml of water in a 500-ml flask, preferably glass-stoppered, add 10 ml of hydrochloric acid (sp gr 1.18) and 1 g of KI. Cool and add 25 ml of 0.03*N* $KMnO_4$ solution which has been standardized against sodium oxalate. Swirl gently, stopper, and let stand for 5 minutes. Titrate the liberated iodine with thiosulphate solution (approximately 0.03*N*) until the color nearly fades. Then add 2 ml of starch solution and continue the titration until the blue color is just destroyed. In another flask, repeat the experiment with the sole difference that 25 ml of the iodate solution is substituted for the standard permanganate solution. The normality of the iodate solution is then found by dividing the volume of $Na_2S_2O_3$ solution required in the second titration by the

[3] Tests indicated that the substitution of hydrogen for air offers no advantages in this particular determination.

[4] If the absorbing solution has warmed up during the evolution, cool it to 20 to 25° C.

volume required in the first, and multiplying by the normality factor of the $KMnO_4$ solution. One ml of N $KMnO_4$=0.01603 g of sulphur.

III. EXPERIMENTAL RESULTS

The accuracy of the procedure was tested on mixtures of CaO, MnO_2, Fe_2O_3, and an amount of ZnS approximately equivalent to the amount of sulphides that may occur in cements. Lime was used in these mixtures because an iron-free portland cement was not available. The results obtained are given in table 1.

TABLE 1.—*Determination of sulphide-sulphur in synthetic mixtures*

ZnS	CaO	MnO_2	Fe_2O_3	Sulphide-sulphur	
				Added [a]	Found
g	g	g	g	g	g
0.0085					0.0027
.0057	3.3			0.0018	.0018
.0052	3.3	0.09		.0017	.0016
.0084	3.3	.09		.0027	.0027
.0080	3.3	.09	0.25	.0026	.0026
.0054	3.3	.09		.0017	([b])

[a] Calculated on the basis of 99.6 percent ZnS.
[b] None found; no $SnCl_2$ added.

The procedure was also applied to several sulphide-bearing portland cements of low manganese content, and to mixtures of these with a cement having a high manganese content. When treated with concentrated hydrochloric acid, 1 g of this cement (labeled *A* in the table) liberated 0.006 g of chlorine per gram, which is in excess of what should be liberated if the manganese were all present in the trivalent state. If all of this chlorine should react with hydrogen sulphide ($H_2S+Cl_2=2HCl+S$), it would destroy 0.0027 g of "sulphide" sulphur. In tests with mixtures of zinc sulphide and the cement it was found that the amount actually destroyed in the evolution method (without stannous chloride) was approximately half theoretical, or about 0.001 g of "sulphide" sulphur per gram of the cement.

The results obtained, together with those obtained in tests in which no $SnCl_2$ was used, were as follows:

	Iodate ml	Sulphur (%)
5 g of cement *A* (0.72% Mn)	0.03	0.000
2 g of cement *B* (5.0% Fe_2O_3; 0.10% Mn)	5.95	.149
2 g of cement *B*+3 g of cement *A*	5.98	.150
2 g of cement *B* (no $SnCl_2$ added)	1.23	.031
2 g of cement *C* (5.3% Fe_2O_3; 0.10% Mn)	1.70	.043
2 g of cement *C*+3 g of cement *A*	1.71	.043
2 g of cement *C* (no $SnCl_2$ added)	.78	.020
4 g of cement *D* (0.3% Fe_2O_3; 0.01% Mn)	1.10	.014
4 g of cement *D*+3 g of cement *A*	1.18	.015
4 g of cement *D* (no $SnCl_2$ added)	.40	.005
4 g of cement *D*+3 g of cement *A* (no $SnCl_2$ added)	.00	None

WASHINGTON, October 24, 1936.

U. S. DEPARTMENT OF COMMERCE NATIONAL BUREAU OF STANDARDS

RESEARCH PAPER RP969

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BROMINE OXIDATION AND MUTAROTATION MEASUREMENTS OF THE ALPHA- AND BETA-ALDOSES *

By Horace S. Isbell and William W. Pigman

ABSTRACT

Rates of oxidation by bromine water, specific rotations, mutarotation coefficients, heats of activation, and other data are reported for α-*d*-glucose, β-*d*-glucose, α-*d*-galactose, β-*d*-galactose, α-*d*-talose, α-*d*-mannose, β-*d*-mannose, mannose $CaCl_2.4H_2O$, α-*d*-gulose $CaCl_2.H_2O$, α-*d*-xylose, α-*d*-lyxose, β-*d*-lyxose, α-*l*-arabinose, β-*l*-arabinose $CaCl_2.4H_2O$, *d*-ribose, *l*-ribose, α-*l*-rhamnose, α-lactose, β-lactose, and β-maltose. The bromine oxidation measurements reveal that the equilibrium solutions are composed for the most part of the normal alpha and beta isomers. Small quantities of other modifications appear to be present in the solutions of arabinose, galactose, talose, and ribose. Fundamental characteristics of the alpha and beta sugars which furnish the basis for the changes in nomenclature previously suggested by Isbell are discussed. It is shown that the sugars which appear as beta modifications under the proposed classification are oxidized by bromine more rapidly than the alpha.

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I. REACTIONS OF THE ALPHA AND BETA SUGARS WITH BROMINE WATER AND A SYSTEM FOR THEIR CLASSIFICATION

An examination of the reaction rates of all the members of a stereomeric series brings out important information relative to the mechanism of the reactions and the structures of the reactive substances which cannot be obtained by other methods. The determination of

*This paper, with the exception of part of the experimental work, is also published in the Journal of Organic Chemistry. A résumé of the general method and the results obtained by the oxidation of the various modifications of glucose, mannose, galactose, lactose, maltose, xylose, arabinose, and rhamnose, was given before the Division of Sugar Chemistry of the American Chemical Society in March 1932 at New Orleans.

the relative reactivity of the various modifications of the sugars is of value in order to understand their reactions in biological systems and in aqueous solutions in general. Previously Isbell and Hudson [1][1] found that the aldose sugars on oxidation with bromine water in slightly acid solution are converted into delta lactones, while Isbell [2] showed qualitatively that the beta sugars are oxidized more rapidly than the alpha sugars, and that the pyranose modifications give delta lactones without the intermediate formation of the free acid. Lippich [3] found that the alpha sugars react with hydrogen cyanide in neutral or alkaline solution slightly more rapidly than the beta sugars. Since the relative rates of reaction for the alpha and beta isomers with bromine and with hydrogen cyanide are different, the reactions do not take place in the same manner. Supposedly the aldehyde modification reacts rapidly with hydrogen cyanide, so that the reaction rate is determined by the rate at which the free aldehyde is formed. On the other hand, the cyclic forms of the sugars are oxidized by bromine water without the intermediate formation of the free aldehyde, so that the reaction rate is not dependent on the rate of aldehyde formation. Our studies [4] with *d*-glucose show that the rate of oxidation of the sugar by bromine water in the presence of barium carbonate is determined by the concentration of the oxidant (free bromine) and by the concentrations and proportions of the alpha and beta modifications of the sugar. The bromine oxidation is particularly suitable for investigation because it gives nearly quantitative yields of the free aldonic acids or their lactones and takes place under conditions such that the change of one sugar to another is slow.

Although there is considerable variation in the reactivity of the separate sugars, the most striking difference is found for the alpha and beta modifications of the same sugar. The existence of the alpha and beta modifications requires the presence of a ring structure and the difference in the reactivity indicates an important structural difference in the two modifications. If the sugars had a uniplanar ring, the oxygen of the ring would lie in the plane of the carbon chain and the alpha and beta positions would be symmetrical with respect to the carbon-oxygen skeleton of the sugar. But if the oxygen and the carbon atoms forming the ring did not lie in one plane [5, 6, and 7] the alpha and beta positions would not be symmetrical with respect to the carbon oxygen skeleton. That is, the alpha and beta positions would be inclined at different angles to the ring and would be influenced to different degrees by the neighboring groups, especially the oxygen. It was pointed out by Isbell [8] that if the sugars are divided into two groups, alpha when the hydroxyl of the first carbon lies in the same direction as the oxygen of the ring, and beta when it lies in the opposite direction, in reactions involving the first carbon atom there is marked similarity in the behavior of all alpha sugars (and derivatives) on the one hand, and of the beta on the other.

The alpha-beta nomenclature most generally used at the present time was originated by Hudson [9]. It has been recognized for a long time that this nomenclature results in classifying as beta those derivatives of *l*-arabinose which exhibit chemical and physical properties similar to the properties of the alpha derivatives of *d*-galactose.

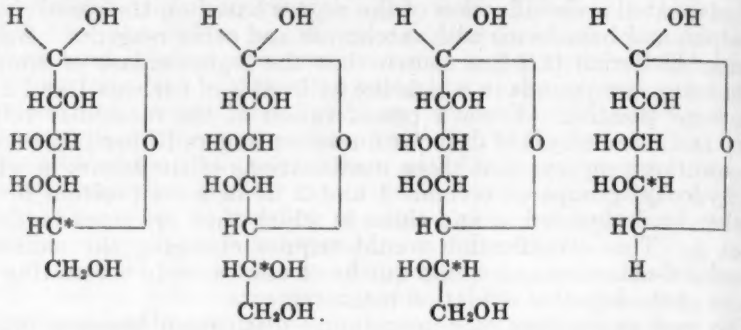
[1] Figures in brackets here and elsewhere in the text correspond to the numbered literature references at the end of this paper.

Several attempts to avoid this confusion have been made and other systems of nomenclature advanced. In 1924 Svanberg and Josephson [11] advocated a classification of the sugars based on the reactivity of the alpha and beta forms with saccharase and other reagents. Subsequently Helferich [12] has shown that the β-glucosidase of emulsin splits many compounds in which the hydroxyls of carbons 1 and 2 are in a *trans* position. From a consideration of the molecular refractivity and other physical data for numerous sugars Riiber [13, 14] and his coworkers suggest that those modifications of the sugars in which the hydroxyl groups of carbons 1 and 2 lie in a *cis* position to one another be designated α, and those in which they are *trans* be designated β. This classification would require changing the names of α- and β-*d*-mannose and would not be of assistance in correlating the results of the bromine oxidation measurements.

The various systems of nomenclature distinguish between optical antipodes by the prefixes *d* and *l*. The substances are allocated to the *d* and *l* series according to the system originated by Rosanoff [10]. Substances in which the hydroxyl on the terminal asymmetric carbon lies to the right are designated *d*, and those in which it lies to the left are called *l*. Thus the antipode of α-*d*-glucose is α-*l*-glucose. This *d* and *l* classification is satisfactory and no changes seem desirable. The change which is advocated is merely the nomenclature of the alpha and beta isomers. Hudson's nomenclature of alpha and beta compounds is based on two factors, the *d* and *l* configuration, and the optical rotation. But there is no relation between the *d* and *l* configuration on the one hand and the structure of the reducing carbon on the other. In the heptose series particularly his nomenclature results in naming the analogs of certain alpha sugars as beta, and vice versa. Isbell overcomes this fundamental defect by taking into consideration another structural characteristic, namely, the configuration of the oxygen ring for differentiating between alpha and beta compounds. Moreover, the oxygen of the ring is united directly with the first carbon and plays an important part in determining the properties of the alpha and beta sugars. By using Hudson's comparison of optical rotations in conjunction with the position of the oxygen of the ring, a system of nomenclature is obtained which is based on the relative positions of all the groups united with the first carbon. The resulting nomenclature can be applied as readily as that in current use and has the distinct advantage that it results in the classification of substances of *like structure and similar properties.*

According to the nomenclature of Hudson the names for the alpha and beta sugars are so selected that "in the *d* series of sugars the more dextrorotatory substance of an α, β pair is designated the α-form, in the *l*-series the more levorotatory one is so named." This nomenclature is not satisfactory because the characterization as α or β depends on whether the sugar belongs in the *d* or *l* series, which in turn depends on the configuration of the terminal asymmetric carbon atom. This key carbon is frequently situated outside of the pyranose ring remote from the group being named. It can be observed from the following formulas that the terminal asymmetric carbon atom (the carbon marked with an asterisk) determines the position of the oxygen ring in the hexoses, as for example in α-*d*-galactose, but in the

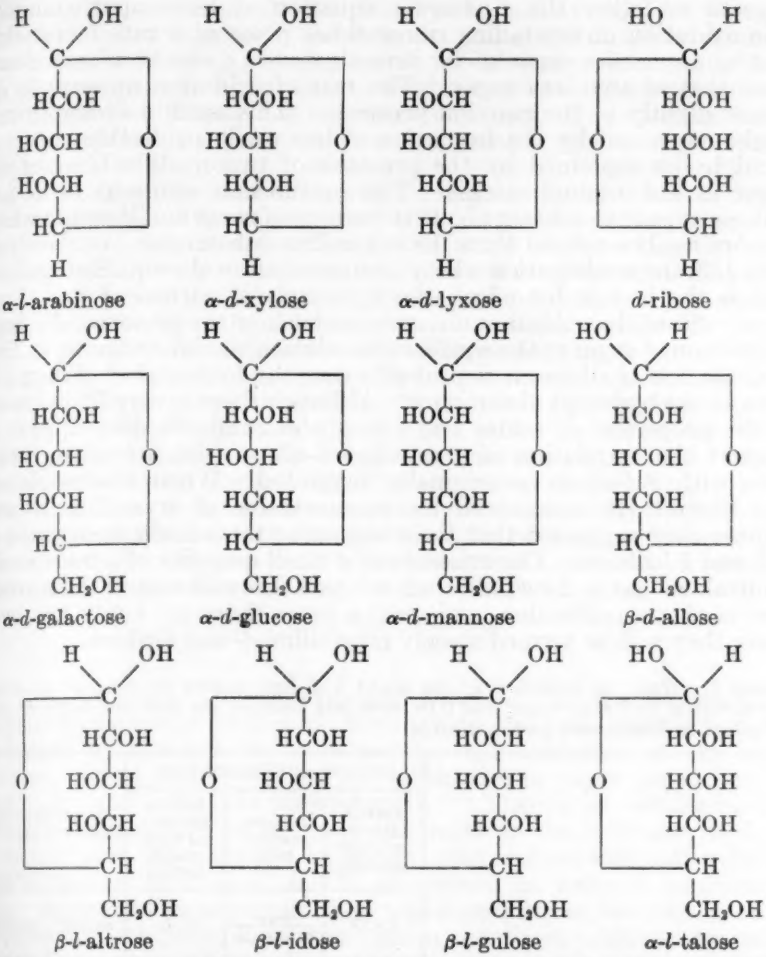
heptoses it lies outside of the pyranose ring and does not have anything to do with the configuration of the first carbon:



α-*d*-Galactose α-*d*-α-Mannoheptose α-*l*-β-Guloheptose α-*l*-Arabinose

In the pentose pyranoses, the terminal asymmetric carbon is not involved in the formation of the oxygen ring and hence it does not have any direct bearing on the configuration of the first carbon. The four sugars illustrated above have the same structure for the pyranose ring and exhibit similar properties, yet according to Hudson's nomenclature two of these are designated alpha and two beta. According to the nomenclature suggested by Isbell [8] all four of these sugars would be designated alpha. *The names of the members of the alpha and beta pair of sugars or sugar derivatives are so selected that when the oxygen ring lies to the right, as in d-glucose, the more dextrorotatory member of the α-β pair shall be designated α, and the less dextrorotatory member β; when the oxygen ring lies to the left, as in l-glucose (or in d-gala-heptose), the less levorotatory member is called β.* This results in names for which the subtraction of the rotation of the beta form from that of the alpha gives a positive difference whenever the oxygen ring lies to the right, and a negative difference when the oxygen ring lies to the left. If the carbon atom united with the hydroxyl forming the oxygen ring is asymmetric, the oxygen of the resulting ring is considered to lie in the direction of the parent hydroxyl. This direction is ascertained by inspection of the Fischer projectional formulas. In the case of the pentoses the direction of the ring is allocated empirically after comparison of their properties with those of sugars with similar configurations. The studies of Hibbert [15], Cox [16], and others show that the oxygen of the ring in the pentose series is not in the plane of the carbon atoms. Therefore, the molecule as a whole is dissymmetric so that it is permissible to postulate structural differences in the alpha and beta pentoses similar to those of the hexoses. In this respect it may be noted that the alpha and beta pentoses reveal differences in the chemical reactions of the first carbon which are analogous to those found for the alpha and beta hexoses.

A comparison of the structures of the pentoses with the hexoses reveals certain similarities which aid in their classification. According to the Fischer projectional method the formulas are represented in the following manner:



It may be observed from these formulas that crystalline *l*-arabinose could be structurally related to either α-*d*-galactose or to β-*l*-altrose. The marked similarity of crystalline *l*-arabinose (+191) to α-*d*-galactose has been stressed by Hudson [17], Riiber [13], and others. The rates of oxidation reported in this paper substantiate the correlation of crystalline *l*-arabinose with α-*d*-galactose and indicate that it should be classified with the alpha sugars. Crystalline *d*-xylose (+94) could be related to either α-*d*-glucose or to β-*l*-idose. It resembles α-*d*-glucose in that it is oxidized slowly and hence it is properly classified as α-*d*-xylose. Crystalline α- and β-*d*-lyxose resemble *d*-mannose rather than *l*-gulose. Since α-*d*-lyxose is oxidized more slowly than β-*d*-lyxose they are properly classified. Classification of crystalline *d*- and *l*-ribose, however, is more perplexing. The *d*-sugar could be structurally related to *l*-talose or to *d*-allose. Ribose [18] gives a rapid and complex mutarotation but the total change is small. The compound character of its mutarotation shows that the equilibrium solution contains at least three modifications. The mutarotation of α-*d*-talose is also complex [19], while the mutarotation of β-*d*-allose [20]

appears to follow the first-order equation at least approximately. The oxidation of crystalline ribose takes place at a rate faster than that of any alpha sugar so far investigated but also at a rate slower than that of any beta sugar. The rate of oxidation appears to decrease slightly as the reaction proceeds. This small decrease in rate might be caused by the formation of less easily oxidizable sugar, or it might be explained by the presence of two modifications of the sugar in the original sample. The equilibrium solutions of *d*- and *l*-ribose appear to contain about 10 percent of some modification which is more easily oxidized than the crystalline substance. As shown on page 153, the modification which predominates in the equilibrium solution is the isomer for which the hydroxyls of carbons 1 and 2 are *trans*. Since the oxidation measurements show the presence of a large proportion of sugar in the equilibrium solution similar to the crystalline modification of ribose, it is probable that the hydroxyl of carbon 1 is *trans* to the hydroxyl of carbon 2. Although there is very little known of the properties of talose and allose, the available data appear to support the correlation of crystalline *d*-ribose with α-*l*-talose rather than with β-*d*-allose as originally suggested. When Phelps, Isbell, and Pigman [18] discovered the mutarotation of crystalline *d*- and *l*-ribose they suggested that these sugars be tentatively designated as β-*d*- and β-*l*-ribose. The existence of a small quantity of a more easily oxidizable sugar in the equilibrium solution throws doubt on the correctness of this classification, and until a more thorough study has been made they will be termed merely crystalline *d*- and *l*-ribose.

TABLE 1.—*Rates of oxidation of the alpha and beta sugars in aqueous solutions containing 0.05 mole sugar and 0.08 mole free bromine per liter and buffered with barium carbonate and carbon dioxide*

Sugar	Oxidation with bromine water			Mutarotation constants at 0.2 ±0.2° C	
	Average value for velocity constant	Relative reaction rates	Ratio of the rates for the α and β isomers		
	$k \times 10^3$	$\frac{k_{sugar}}{k_{\alpha\text{-}d\text{-}glucose}}$	k_β/k_α	$m_1 \times 10^3$	$m_2 \times 10^3$
α-*d*-Glucose	32	1	39.2	0.741	
β-*d*-Glucose	1,255	39		.738	
α-*d*-Mannose	51	1.6	15.3	2.16	
β-*d*-Mannose	781	24		2.14	
α-*d*-Galactose	42	1.3	37.9	0.93	11.9
β-*d*-Galactose	1,590	50		.90	16.7
α-*d*-Talose	78	2.4	10.8	3.62	25.5
β-*d*-Talose (from equilibrium solution)	844	26			
α-*d*-Gulose $CaCl_2.H_2O$	71	2.2	5.9	1.88	
β-*d*-Gulose (from equilibrium solution)	418	13			
α-*l*-Arabinose	95	3.0	17.5	3.62	21.7
β-*l*-Arabinose $CaCl_2.4H_2O$	1,658	52		3.84	36.9
α-*d*-Xylose	90	2.8	18.6	2.45	
β-*d*-Xylose (from equilibrium solution)	1,673	52			
α-*d*-Lyxose	156	4.9	2.9	8.44	
β-*d*-Lyxose	449	14		8.40	
d-Ribose (crystalline)	196	6.1	5.2		
β-*d*-Ribose (from equilibrium solution)	1,010	32			
l-Ribose (crystalline)	195	6.1	7.5	6.87	54.0
β-*l*-Ribose (from equilibrium solution)	1,456	45.5			
α-*l*-Rhamnose, hydrate	90	2.8	8.6	5.68	
β-*l*-Rhamnose (from equilibrium solution)	770	24			
α-Lactose, hydrate	29	0.9	32.8	0.54	
β-Lactose	952	30		.52	
α-Maltose (from equilibrium solution)	24	0.8	64		
β-Maltose, hydrate	1,528	48		.58	

It may be seen from the results given in table 1 that if the sugars are classified as suggested, the beta isomers are oxidized by bromine more rapidly than the alpha isomers. This generalization is based on all the sugars so far investigated, which include the alpha and beta modifications of five of the eight pyranose types. Measurements on the idose, allose, and altrose types are necessary, however, before it is certain that the generalization applies to all pyranose sugars.

The study of the mechanisms of the reactions is complicated by the interconversion of the various modifications which exist in the aqueous solutions. The mutarotation reaction which occurs when the sugar is dissolved in water results in the formation of either more or less easily oxidizable modifications. The production of a less readily oxidizable substance retards the rate of oxidation, while the formation of more readily oxidizable substance accelerates the rate. Thus the reaction of the alpha sugars with bromine water can be considered to consist in two simultaneous reactions. One of these is the oxidation of the alpha sugar directly, and the other the conversion of the alpha sugar to beta or other easily oxidizable substance and the subsequent oxidation thereof. In the oxidation of α-*d*-glucose it was shown [4] that if the concentration of the oxidant (free bromine) is held constant, and if it is assumed that the beta sugar is oxidized as fast as it is formed, the usual formula for two simultaneous reactions gives the equation

$$k_1+ak_\alpha=\frac{1}{t}\ln\frac{A}{A-X}.$$

In this equation k_1 is the velocity constant for the conversion of α-glucose to easily oxidizable sugar, a is the concentration of free bromine, k_α the velocity constant for the oxidation of the alpha isomer, and A and $A-X$ are the quantities of sugar present at the beginning and end of the time interval, t. There is no reliable method for determining k_1. In our previous paper on the oxidation of *d*-glucose its value was assumed to be the same as that obtained from the mutarotation coefficient, k_1+k_2 (expressed in natural logarithms). This represents an approximation which permits an evaluation of the relative importance of the mutarotation and direct oxidation reactions. Since the mutarotations of many sugars are complex, the value of k_1 cannot be determined even approximately, and consequently a correction for the mutarotation reaction is not feasible. In certain cases the oxidation of the beta isomers is less rapid than that of glucose, and hence the assumption that the beta isomer is oxidized as rapidly as it is formed is not justified. For these reasons the reaction rates for the alpha and the beta sugars were calculated, using common logarithms, by the simple formula

$$ak=\frac{1}{t}\log\frac{A}{A-X}$$

without attempting to make a correction for the mutarotation reaction.

It can be seen from the data of table 1 that the pentoses, with the exception of β-*d*-lyxose, are oxidized more readily than the corresponding hexoses. The more rapid oxidation of the alpha pentoses is probably caused by the more rapid mutarotation reaction with the accompanying production of easily oxidizable modifications; the less rapid oxidation of β-*d*-lyxose may result from a similar cause, the formation

of the less readily oxidizable alpha modification. The values for the mutarotation constants, m_1 and m_2, are given in table 1 so that the reader can judge for himself the importance of these reactions in the interpretation of the oxidations. The constants, m_1 and m_2, were obtained as described on page 156. m_1 is the same as the mutarotation coefficient, k_1+k_2, calculated for the later part of the mutarotation; m_2 also represents the sum of several constants which individually cannot be satisfactorily evaluated.

It will be noted that the velocity constants given for β-*d*- and *l*-ribose do not agree closely. These constants were obtained from a very rapid reaction involving only 10 percent of the sugar in the equilibrium solution and consequently the experimental error is large and the values are only approximate.

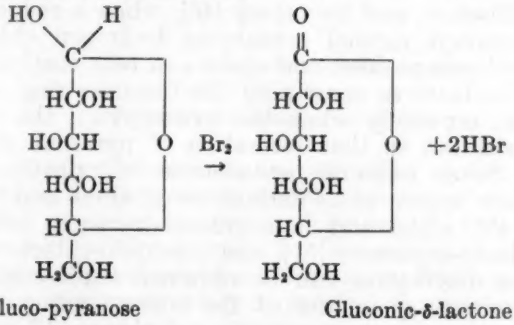
It can be seen from the data in table 1 that α-*d*-galactose is oxidized slightly more rapidly than α-*d*-glucose but less rapidly than β-*d*-glucose, while β-*d*-galactose is oxidized more rapidly than either α- or β-*d*-glucose. The properties of the alpha and beta modifications of *d*-galactose and *d*-glucose in the equilibrium solutions are such that the oxidation of the equilibrium solution of *d*-galactose is more rapid than that of *d*-glucose. Hence our results confirm and extend the observation [21] that *d*-galactose is oxidized by bromine water more rapidly than *d*-glucose. It may be noted also that α-*d*-talose, α-*d*-mannose, and α-*d*-gulose $CaCl_2.H_2O$ are oxidized more rapidly than α-*d*-glucose. On the other hand, the corresponding equilibrium solutions are initially oxidized more slowly than the equilibrium solution of glucose, while in the latter stages they are oxidized more rapidly. Therefore it is evident that a comparison of the reaction rates should not be made in general terms. Although several relationships between the configurations and the rates of reaction are apparent, such comparisons will be held in abeyance until sugars containing the allose, altrose, and idose structures have been investigated.

II. COMPOSITION OF EQUILIBRIUM SUGAR SOLUTIONS

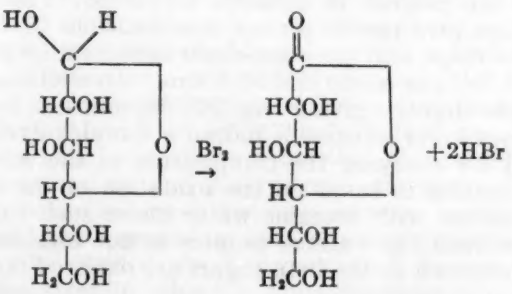
In 1846, Dubrunfaut [22] discovered that when glucose is dissolved in water the optical rotatory power of the solution decreases on standing until finally it reaches a constant value. Subsequently Pasteur [23, 24], Erdmann [25], Urech [26], and others [27] found that the optical rotations of freshly prepared solutions of the reducing sugars in general change on standing, a phenomenon which came to be known as mutarotation. In the beginning Dubrunfaut suggested that the change in optical rotation is caused by a change in molecular structure, but at that time the structures of even simple organic compounds were not known. The aldehyde structure for glucose was suggested by Von Baeyer in 1870 [28], but it did not satisfactorily represent the experimental facts because the sugar did not give the characteristic aldehyde reactions. In order to explain the absence of these reactions Colley [29] postulated an ethylene oxide structure and Tollens [30] a butylene oxide structure. It was pointed out by Von Lippman [31] that the first carbon in the cyclic sugar is asymmetric and that two stereomeric isomers are possible. Erdmann [25] had previously prepared two forms of lactose, one having a higher rotation than the stable solution and the other a lower rotation. Modifications of similar character were found for numerous sugars by Tanret [32] and others. A ring structure is necessary to account for these isomeric forms, and for the two methyl glucosides prepared by Fischer [33].

These glucosides did not give the aldehyde reactions and apparently contained ring structures. Because they resembled the gamma lactones they were assigned a 1,4 ring structure and erroneously considered as such, until later work by Haworth [34] and others established that they contain the 1,5 or pyranose ring. In the meantime other glycosides had been prepared which do contain the 1,4 or furanose ring [35] so that there are two series of glycosides containing different ring structures. Supposedly, the 1,4 ring modifications of the sugars also exist but little is known about the proportions of these in aqueous solutions or of their part in the mutarotation reaction. Because products corresponding to both ring types are obtained by methylation of the sugars [36], other methods must be used to ascertain their structure.

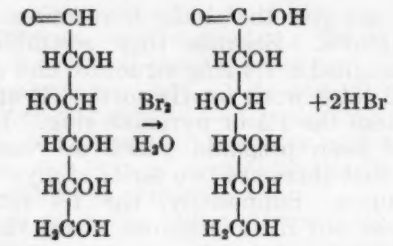
The methods for determining the ring structure of the sugars are (1) a comparison of the optical rotations of the sugars with the optical rotations of the corresponding methyl glycosides whose structures are known [37, 38, 39, 40]; (2) a correlation of the methyl glycosides with the alpha and beta sugars by enzymatic hydrolysis [41]; (3) a measurement of the direction of the optical rotation of a solution containing equivalent quantities of the alpha and beta isomers [42]; (4) a comparison of the X-ray diffraction patterns of crystalline sugars and crystalline glycosides of known structure [43]; and (5) a study of various chemical reactions under conditions such that the rate of change from one form of the sugar to another is slow, as in the oxidation of the sugars with bromine water in the presence of a suitable buffer. According to the last method [1, 2] delta lactones are obtained by the oxidation of pyranoses, gamma lactones from furanoses, and supposedly free acids from aldehyde sugars. The reactions are represented by the following equations:



β-*d*-Gluco-pyranose — Gluconic-δ-lactone



β-*d*-Gluco-furanose — Gluconic-γ-lactone



Aldehydo-glucose Gluconic acid

The results obtained by one of us [2] with α- and β-*d*-glucose, α- and β-*d*-mannose, α- and β-*l*-rhamnose, α- and β-lactose, β-cellobiose, and β-maltose show that on oxidation with bromine these sugars give delta lactones. Mannose $CaCl_2.4H_2O$, however, gives mannonic gamma lactone and presumably has the furanose structure [44]. The information thus derived shows that the crystalline sugars which have been investigated, with the exception of mannose $CaCl_2.H_2O$, have the pyranose structure. The results obtained by the other methods also lead to this conclusion, but since *d*-talose, *d*-ribose, and *l*-ribose have not been extensively studied the allocation of the pyranose structure to these is entirely arbitrary.

The spontaneous crystallization of the alpha and beta pyranoses, the course of the mutarotation reactions, the solubility measurements with the crystalline sugars [45], and the bromine oxidation method indicate that the pyranose modifications comprise by far the largest part of the sugar in solution. Nevertheless, the complex character of the solutions is plainly apparent from the numerous products which can be derived from reaction with various reagents. As shown by Fischer, and by others [46], when a reducing sugar is treated with methyl alcohol containing hydrogen chloride, alpha and beta methyl pyranosides, and alpha and beta methyl furanosides are formed. Derivatives containing the furanose ring are given by other reactions, especially when the hydroxyl on the first or fifth carbon is substituted so that formation of pyranose derivatives is not possible. Seven isomeric pentacetates of galactose are known products. These appear to be derivatives of alpha and beta galactofuranose [47, 48], alpha and beta galacto-pyranose [49, 50], alpha and beta *d*-galacto-septanose [51], and aldehydo-galactose [52]. The fact that these derivatives can be obtained lends credence to the concept that minute quantities of the corresponding modifications of the sugars are present in aqueous solutions. The various ring isomers may also give rise to several modifications [5, 6] containing strainless Sache rings, and the open-chain isomers may exist partially in hydrated [53, 54] and enolic [55, 56] forms. In addition to these the sugars dissociate slightly, giving ions [57, 58] and free hydrogen [59]. Thus an aqueous sugar solution is indeed a complex dynamic system.

The method for studying the composition of the solutions in the present investigation is based on the oxidation of the sugars in the equilibrium mixture with bromine water under such conditions that equilibrium between the various isomers is not established prior to oxidation. Inasmuch as the beta sugars are oxidized rapidly and the

alpha sugars slowly, the proportion of the beta isomer in the original solution cannot exceed the proportion of the easily oxidizable substance, and the proportion of the alpha cannot exceed the proportion of the slowly oxidizable material. It was shown previously [4] that about 64 percent of the sugar present in the equilibrium solution of glucose is oxidized rapidly at a rate comparable to the oxidation of β-*d*-glucose, and 36 percent is oxidized slowly at a rate comparable to the oxidation of the alpha isomer. Since these proportions agree with the amounts of α- and β-*d*-glucose estimated from the rotation of the solution, and calculated on the assumption that the solution contains only two isomers, it appears that the equilibrium solution of glucose contains, at least largely, the alpha and beta normal forms.

Application of this method to numerous equilibrium solutions of sugars has shown that a portion of the sugar in each case is oxidized

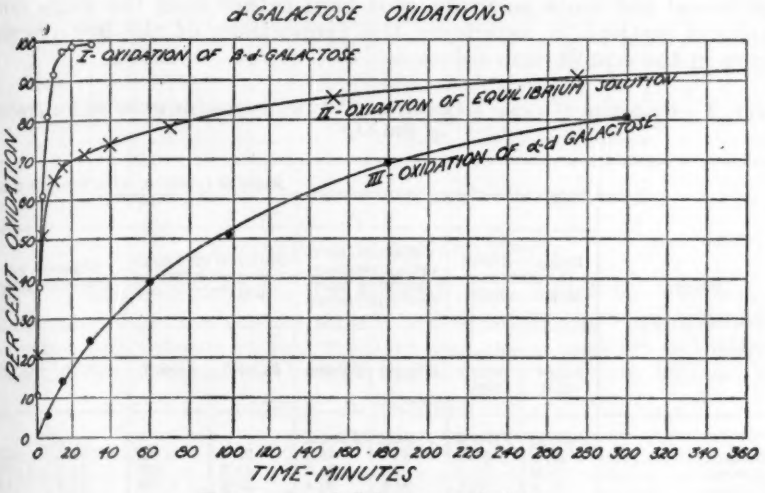

d-GALACTOSE OXIDATIONS
I- OXIDATION OF β-d-GALACTOSE
II- OXIDATION OF EQUILIBRIUM SOLUTION
III- OXIDATION OF α-d GALACTOSE
PER CENT OXIDATION
TIME-MINUTES
0 20 40 60 80 100 120 140 160 180 200 220 240 260 280 300 320 340 360

FIGURE 1.—*d-Galactose oxidations.*

rapidly at a rate comparable to the oxidation of the corresponding beta sugar, while the remainder is oxidized slowly at a rate corresponding to that of the alpha sugar. This can be seen by the results illustrated for *d*-galactose in figure 1. The oxidation of β-*d*-galactose is rapid and virtually complete in 20 minutes, while α-*d*-galactose requires 5 hours for approximately 80 percent of oxidation. The equilibrium solution supposedly containing these constituents is oxidized rapidly for about 20 minutes and then more slowly. When the percentage of oxidation is expressed on a logarithmic scale, the oxidation curve should be linear for a first-order reaction, or for a second-order reaction in which the concentration of the oxidant is maintained constant. In figures 2 and 3 the oxidations of lactose and *d*-mannose are given on such a scale. It will be noted that the curves representing α- and β-lactose and α- and β-*d*-mannose are approximately linear. The small curvature is largely due to a decrease in the concentration of the oxidant, free bromine, as the reaction progressed. This explanation may be verified by an inspection of the velocity constants for these sugars given in table 7. Thus the value of k obtained after correction for the variation in the free bromine concentration is more nearly constant than the uncorrected constant, ak. For α-*d*-gulose,

α-*d*-galactose, and α-*d*-xylose the drifts in the velocity constants (see table 7) appear to be slightly larger than the experimental error. This may be due to an accumulation of unknown, less readily oxidizable modifications of the sugars in the solution, or to the production of other products which interfere with the analytical method.

The latter portion of the curves for the oxidation of the equilibrium solutions of lactose and *d*-mannose parallel those for the corresponding alpha isomers when the semilog scale is used as in figures 2 and 3. The equal slopes indicate that the reactions proceed at equal rates. Extrapolation of the portion of the curve representing the oxidation of the less reactive sugar as represented by the dotted line to zero time, gives the logarithm of the less reactive sugar at zero time. The extrapolation can be conducted graphically, or mathematically as described on page 177. Because the mathematical extrapolation is impersonal and more accurate, it is used rather than the more rapid graphical method to determine the proportions of the less reactive sugars in the equilibrium solutions.

TABLE 2.—*Oxidation of sugar solutions at* 0° C *with bromine water in the presence of* $BaCO_3$[a]

Sugar	Composition of equilibrium solution				Rates of oxidation with bromine water at 0° C			
	Estimated from the oxidation measurements		Calculated from optical rotations assuming only two constituents		Obtained with equilibrium solutions at 0.3° C		Obtained with crystalline sugars	
	Less reactive sugar	More reactive sugar	α-Sugar	β-Sugar	$k_A \times 10^3$	$k_B \times 10^3$	$k_\alpha \times 10^3$	$k_\beta \times 10^3$
	Percent	*Percent*	*Percent*	*Percent*				
d-Glucose	37.4	62.6	36.2	63.8	27.5	1,362	32.4	1,255
d-Mannose	68.9	31.1	68.8	31.2	45.2	860	51.1	781
d-Galactose	31.4	68.6	29.6	70.4	37.9	1,720	42.3	1,500
d-Talose	55.9	44.1	----------	----------	84.8	844	78.5	----------
(*d*-Gulose)$_2$ $CaCl_2.H_2O$	18.5	81.5	----------	----------	52.6	418	54.8	338
l-Arabinose	32.4	67.6	26.5	73.5	84.2	1,608	95.3	1,658
d-Xylose	32.1	67.9	[b]34.8	[b]65.2	80.3	1,673	89.9	----------
d-Lyxose	79.7	20.3	76.0	24.0	189	717	156	449
d-Ribose	89.3	10.7	----------	----------	180	1,010	196	----------
l-Ribose	89.0	11.0	----------	----------	170	1,456	195	----------
l-Rhamnose	69.0	31.0	[b]73.1	[b]26.9	83.4	770	89.7	----------
Lactose	37.5	62.5	36.8	63.2	20.9	1,475	29.3	952
Maltose	37.7	62.3	[b]36.0	[b]64.0	23.7	1,388	----------	1,528

[a] The experimental details for the oxidation measurements are given on page 173 and for the optical rotations on page 158.

[b] Percentage calculated from Hudson's optical rotations derived from measurements of the initial and final solubilities at 20° C (BS Sci. Pap. 21, 267 (1926) S533.

It may be observed from the data given in table 2 that the proportions of the less reactive and more reactive sugars do not differ widely from the hypothetical proportions of the alpha and beta sugars, which were calculated from the optical rotations by assuming that the equilibrium solutions contain only normal alpha and beta isomers. Inasmuch as all of the less reactive sugar is not necessarily alpha, nor all of the more reactive, beta, the proportions of the less reactive and of the more reactive sugar represent limiting values for the alpha and beta normal sugars rather than absolute values. The striking agree-

ment of the proportions obtained from the oxidation studies with those obtained from the optical measurements, however, makes it seem probable that the equilibrium solution consists, at least largely, of the normal alpha and beta isomers.

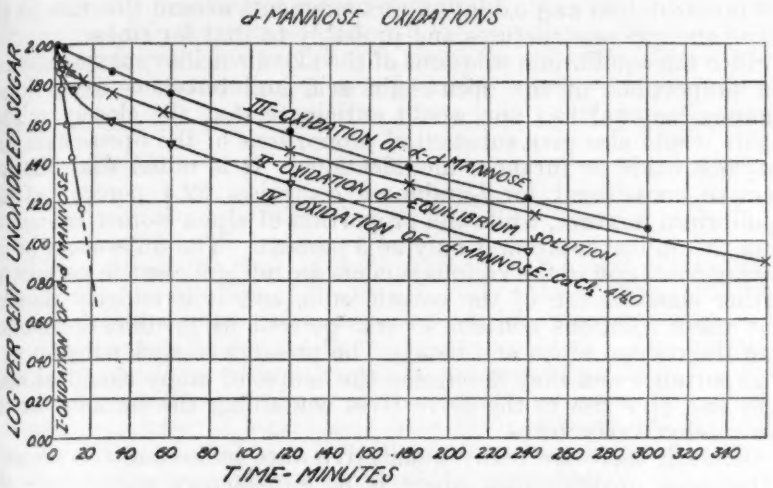


FIGURE 2.—*d-Mannose oxidations.*

It may be observed from the data of table 2 that the equilibrium solutions of sugars of similar structure frequently have approximately the same proportions of less reactive and more reactive substances. Thus the proportions of the two fractions for glucose, lactose, and

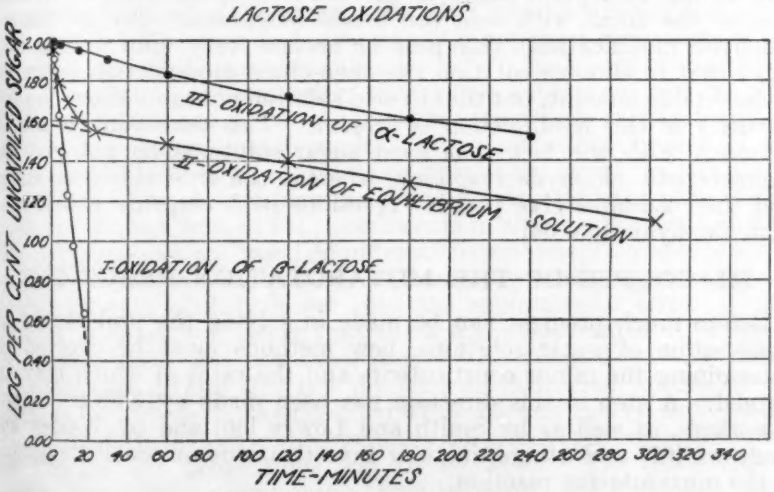


FIGURE 3.—*Lactose oxidations.*

maltose are nearly the same. Also the proportions for galactose and arabinose and for mannose and rhamnose are alike, while the proportions for xylose, lyxose, and ribose differ slightly from those for glucose, mannose, and talose, respectively. For every sugar so far investigated, the less reactive modification (the alpha form according to the suggested nomenclature) predominates in the equilibrium solution

whenever the hydroxyl of carbon 2 is directed away from the ring. This generalization is in agreement with the statement of Haworth and Hirst [108] "that in the equilibrium mixture of the two isomerides the tendency is for the *trans* form to predominate." The results of our mutarotation and oxidation measurements extend this rule to the talose and gulose structures and probably to that for ribose.

Since the equilibrium solutions of the aldonic acids contain substantial proportions of the open-chain acid and butylene oxide forms (gamma lactone) [60] one would anticipate that the closely related sugars would also give substantial proportions of the open-chain and butylene oxide or furanose modifications. It is noted that the less reactive constituent for *l*-arabinose comprises 32.4 percent of the equilibrium mixture, while the proportion of alpha isomer calculated from the optical rotation is only 26.5 percent. The differences in the rates of oxidation of the various isomers are not sufficient to permit the further classification of the constituents, and it is entirely possible that these solutions contain several percent of modifications other than the normal alpha and beta. The presence of such substances is of importance and may determine the course of many chemical reactions and give rise to the derivatives containing the furanose or the free aldehyde structures.

Although there are many qualitative data indicating the presence of furanose modifications, there is no satisfactory method for the identification and estimation of these modifications, but fortunately the presence or absence of even a small quantity of the aldehyde modification can be ascertained with certainty. Thus it has been shown by Gabryelski and Marchlewski [61] and others [62] that glucose, galactose, maltose, arabinose, and rhamnose in alkaline solution give strong absorption bands in the ultraviolet, but after neutralization of the alkali with acid the bands (supposedly due to the free aldehyde modification) disappear or become very faint. This indicates that in alkaline solution the open-chain modification is present in detectable amount, but that in acid solution not more than a minute quantity of this modification is present. This conclusion is also in harmony with the fact that most sugar solutions do not give the characteristic aldehyde reactions, whereas the true aldehyde sugars and their acetates give positive reactions with reagents which react with aldehydes [63, 64].

III. COURSE OF THE MUTAROTATION REACTIONS

Before much progress can be made in solving the problem of the composition of sugar solutions, new methods must be evolved for determining the minor constitutents and the rates at which they are formed. A step in this direction has been made by Riiber [65] and coworkers, as well as by Smith and Lowry [66] and by Worley and Andrews [67] and others, in their investigations on small deviations in the mutarotation reaction.

The mutarotation measurements of Trey [72], Osaka [73], and other early investigators appeared to follow the first-order or unimolecular law. According to this law, the optical rotation at any time after dissolving the sugar in water can be expressed by the equation

$$[\alpha]_D = Ae^{-kt} + C, \tag{1}$$

in which $[\alpha]_D$ is the specific rotation at the time t, e the logarithmic base, A the difference between the initial and final specific rotations,

C the final or equilibrium specific rotation, and k the velocity constant for the change in rotation. In 1899 Lowry [69] (see also Hudson [68]) suggested that the mutarotation reaction was a reversible one, and in 1903 Hudson [70] showed that the two forms of lactose have equal velocity constants for their mutarotations, and that the maximum rate of solution is in accord with the hypothesis that the changes in rotation are not due to different reactions but to opposite parts of one balanced reaction. By applying the mass action law to the reversible reaction represented as $\alpha \underset{k_2}{\overset{k_1}{\rightleftarrows}} \beta$ Hudson [71] developed the following equation:

$$k_1+k_2=\frac{1}{t}\log\frac{r_o-r_\infty}{r_t-r_\infty}, \qquad (2)$$

in which t equals the time after dissolution, r_0 the optical rotation at zero time, r_t the rotation at the time t, and r_∞ the final or equilibrium rotation. The mutarotation coefficient, k_1+k_2, was shown to be the sum of the constants for the two opposing reactions. The mutarotation coefficient is usually expressed in common logarithms, but if the values of k_1 and k_2 are to be applied in kinetic problems they must be reduced to a natural logarithmic base by multiplication by 2.3026. This equation is merely the logarithmic form of equation 1 expressed in terms of the observed rotations and the separate velocity constants.

Until relatively recently it was believed that the monomolecular equation adequately represents the mutarotation of the reducing sugars. In 1926 Riiber and Minsaas published a paper [65] on the existence of a third modification of galactose in which they showed that during the mutarotation of alpha and beta galactose the changes in refractive index and molecular volume give evidence for at least three modifications of the sugar. Shortly afterwards Smith and Lowry [66] as well as Worley and Andrews [67] reported deviations in the mutarotation of α- and β-d-galactose which had been neglected by earlier workers. By assuming that three substances are involved Riiber and Minsaas developed an equation which satisfactorily expresses their experimental results. By a somewhat similar process Smith and Lowry applied equations previously developed by Lowry and John [74] to their measurements and calculated the optical rotations and proportions of the constituents in the equilibrium solutions. The calculations were based on different hypothetical three-component systems, on the measurement of different physical properties, and on deviations only slightly larger than the experimental error. Consequently it is not surprising that there was considerable difference in the results from the two laboratories. As pointed out by Riiber, Minsaas, and Lyche [75] the proportions estimated by Riiber and Minsaas, as well as those calculated by Smith and Lowry, are based on the assumption that only three isomers are present; if more substances are present the proportions will be incorrect. The prevalence of equilibrium systems containing three or more constituents is shown by recent work. Thus Dale [76] reported a calcium chloride compound of mannose which exhibits a complex mutarotation, while Phelps, Isbell, and Pigman [18] and Isbell [77] showed that d- and l-ribose and d-β-glucoheptose give similar mutarotations. The compound character of these mutarotations clearly shows that the reactions are more complex than the simple interconversion of two isomers,

and that it is necessary to adopt a method for expressing the mutarotation which takes account of these characteristic properties.

Smith and Lowry's fundamental equation for expressing the complex mutarotations is difficult to apply because it involves numerous constants which must be determined by laborious mathematical calculations. The evaluation of these constants requires the postulation of a definite number of reactions taking place in a certain manner so that values thus obtained are highly speculative. The fundamental equation was simplified by them to the following form:

$$[\alpha]_D = Ae^{-m_1't} + Be^{-m_2't} + C. \tag{3}$$

This equation satisfactorily represents two consecutive reactions as $x \rightleftarrows y \rightleftarrows z$. As applied to the sugar series the equation is more or less empirical, but it appears to fit the data for the simple and complex mutarotations as completely as the monomolecular equation fits the simple alpha-beta interconversions. Term C in equation 3 represents the equilibrium rotation, A the total change in optical rotation due to the slow or principal mutarotation reaction, and B the deviation between the initial rotation and that obtained by extrapolation of the slow mutarotation to zero time.

The exponents m'_1 and m'_2 are functions of the velocity constants for the separate reactions which occur during the mutarotation and represent the rate at which the optical rotation changes. The equation can be conveniently expressed to the base 10 rather than e, in which case m_1 and m_2 are in common logarithms rather than in natural logarithms.

In order to develop equations of this type from the experimental data by the method of Lowry and Smith [78] the mutarotation is divided into two periods, a short period, beginning at zero time during which a rapid change occurs, and a long period, beginning when the rapid change is substantially complete. By applying the formula

$$m_1 = \frac{1}{t_2 - t_1} \log \frac{r_1 - r_\infty}{r_2 - r_\infty} \tag{4}$$

to the data representing the long period (that is, the last part of the mutarotation) values of m_1 are obtained. It will be observed that m_1 is the ordinary mutarotation coefficient measured for the latter part of the mutarotation, and that a mutarotation which follows the unimolecular law gives rise to only one exponential term. The constant, m_2, for the initial rapid change is calculated from the following equation:

$$m_2 = \frac{1}{t_2' - t_1'} \log \frac{d_1}{d_2}, \tag{5}$$

in which d_1 and d_2 represent the differences between the observed rotations and those obtained by extrapolation of the long period back to the corresponding times. The extrapolation is accomplished mathematically by substitution of the calculated value of m_1, the observed equilibrium rotation, r_∞, and the observed rotation, r_2, at the time, t_2, selected after the rapid period is over, in equation 4, and solving for the rotation, r_1, at the desired time, t_1.

The following example based on the data for the mutarotation of *α-l*-arabinose at 0° C, reported in table 11, page 184, is given to clarify this description. Column 2 gives the observed rotations at the indicated times. The calculation of m_1 is begun at 60.4 minutes, since calculations started at earlier times give a drift in the constant. The values of m_1 given in column 4 are obtained by application of equation 4 using $r_1=75.01$, $t_1=60.4$, and for r_2, readings taken at later times. The slow reaction is carried back to times earlier than 60.4 minutes by substituting the average value of m_1 (3.62×10^{-3}) in equation 4 and solving for r_1 at each of the times, t_1, earlier than 60.4 minutes (including zero time), using $r_2=75.01$, $r_\infty=52.20$, and $t_2=60.4$. (The equilibrium rotation, subtracted from the calculated value at zero time, gives A in equation 6.) These values, subtracted from the observed rotations at the corresponding times, give the deviations shown in column 5 of the table. The constant, m_2, for the rapid change is then obtained by substituting the deviations in equation 5, using $d_1=2.28$, $t'_1=4.3$, and for d_2 successively each of the values recorded at the later times, t'_2, and solving for m_2. By placing the average value of m_2 (21.7×10^{-3}) in equation 5, and using $d_2=2.28$ and $t_2=4.3$, the value of d_1 at zero time, t_1, may be obtained by solution of the equation. The value so obtained (2.83) is that to be used for B in the following equation:

$$°S=A\times10^{-m_1t}+B\times10^{-m_2t}+C. \qquad (6)$$

The equilibrium rotation (52.20) is C, while A, as already explained, is 37.74. Substitution of these values in equation 6 gives

$$°S=37.74\times10^{-0.00362t}+2.83\times10^{-0.0217t}+52.20. \qquad (7)$$

If it is desired to use the natural logarithmic base, equation 7 would be changed only by replacement of the base "10" by "*e*" and by multiplying each of the exponents by 2.3026. This equation is converted to a specific rotation basis by multiplying by the ratio of the equilibrium specific rotation to the observed equilibrium rotation in sugar degrees (°S).

In this paper the mutarotations of sugars which follow the unimolecular course within the experimental error are expressed by the equation containing only one exponential term, while those which deviate considerably from the unimolecular course are expressed by equations containing two exponential terms. A summary of the results is given in table 3. The experimental procedure and the data are reported in more detail on page 178.

TABLE 3.—*Summary of optical-rotation measurements made in this investigation*

1	2	3	4	5	6	7	8	9
Sugar	Concentration	Temperature	Initial	Equilibrium	Molecular rotation	Hudson's 2A	$[\alpha]_D$ at t minutes after dissolving crystals	References to related data
	g/100 ml	°C	$[\alpha]_D$	$[\alpha]_D$	$[M]$	$[M]_\alpha - [M]_\beta$		
β-d-Glucose	3.9	20.0	+112.2	+52.7	+20,210	+16,840	$+59.5\times10^{-.006231t}+52.7$	[100, 101]
α-d-Glucose	3.9	0.2	+111.5	+52.1	+20,080	+16,770	$+59.4\times10^{-.000741t}+52.1$	[81, 90]
β-d-Glucose	3.9	20.0	+18.7	+52.7	+3,370	----------	$-34.0\times10^{-.006231t}+52.7$	[102, 103]
δ-d-Glucose	3.9	0.2	+18.4	+52.1	+3,310	----------	$-33.7\times10^{-.000739t}+52.1$	[81, 67]
α-d-Galactose	5.0	20.0	+150.7	+80.2	+27,150	+17,640	$+64.9\times10^{-.006931t}+5.6\times10^{-.07904t}+80.2$	[65, 78]
α-d-Galactose	4.1	0.0	+152.9	+84.0	+27,540	+17,630	$+66.3\times10^{-.0000301t}+2.7\times10^{-.01191t}+84.0$	[66, 67]
β-d-Galactose	4.0	20.0	+52.8	+80.2	+9,510	----------	$-32.3\times10^{-.006131t}+4.9\times10^{-.0883t}+80.2$	[78, 75]
δ-d-Galactose	4.1	0.0	+55.0	+84.0	+9,910	----------	$-31.5\times10^{-.0006971t}+2.5\times10^{-.0167t}+84.0$	[66]
α-d-Mannose	4.0	20.0	+29.3	+14.2	+5,280	+8,340	$+15.1\times10^{-.01731t}+14.2$	[104, 105]
α-d-Mannose	4.0	0.2	+28.8	+14.6	+5,190	+8,200	$+14.2\times10^{-.002161t}+14.6$	[104]
β-d-Mannose	4.0	20.0	−17.0	+14.2	−3,060	----------	$-31.2\times10^{-.01731t}+14.2$	[89, 45]
β-d-Mannose	4.0	0.3	−16.7	+14.6	−3,010	----------	$-31.3\times10^{-.002161t}+14.6$	[89, 104]
Mannose $CaCl_2.4H_2O$	9.1	20.0	−31.3	+6.0	−11,370	----------	$+4.0\times10^{-.02451t}-41.1\times10^{-.3111t}+6.0$	[76]
Mannose $CaCl_2.4H_2O$	8.4	0.0	−29.7	+6.2	−10,790	----------	$+4.5\times10^{-.003571t}-40.3\times10^{-.0566t}+6.2$	[76]
α-d-Talose	3.8	20.0	+68.0	+20.8	+12,250	----------	$+9.3\times10^{-.02531t}+37.9\times10^{-.1351t}+20.8$	[106, 19]
α-d-Talose	4.0	0.1	+62.5	+25.2	+11,260	+9,870	$+9.8\times10^{-.006331t}+27.5\times10^{-.0855t}+25.2$	[19]
β-d-Talose[b]	4.0	20.0	+13.2	+21.0	+2,380	----------	$-17.5\times10^{-.02531t}+9.7\times10^{-.1011t}+21.0$	----------
α-d-Gulose $CaCl_2.H_2O$	6.807	20.0	+37.1	−10.0	+11,470	----------	$+47.1\times10^{-.01811t}-10.0$	[82]
α-d-Gulose $CaCl_2.H_2O$	6.468	0.2	+40.5	−9.4	+12,520	----------	$+49.9\times10^{-.001891t}-9.4$	----------
$(d\text{-Gulose})_2\ CaCl_2.H_2O$	4.281	20.1	+29.4	−16.5	•+7,190	----------	$+45.9\times10^{-.0197t}-16.5$	[83]
$(d\text{-Gulose})_2\ CaCl_2.H_2O$	4.215	0.2	+34.6	−16.9	•+8,460	----------	$+51.5\times10^{-.002021t}-16.9$	----------
α-l-Arabinose	4.3	20.0	+190.6	+104.5	+28,610	+17,050	$+77.3\times10^{-.0309t}+8.8\times10^{-.1334t}+104.5$	[14, 93]
α-l-Arabinose	4.1	0.0	+194.0	+109.2	+29,120	+17,330	$+78.9\times10^{-.003431t}+5.9\times10^{-.0217t}+109.2$	[19]
β-l-Arabinose $CaCl_2.4H_2O$	8.9	20.0	+34.7	+48.0	+11,560	----------	$-16.8\times10^{-.0309t}+3.5\times10^{-.1094t}+48.0$	[92, 93]
β-l-Arabinose $CaCl_2.4H_2O$	9.3	0.0	+35.4	+50.1	+11,790	----------	$-16.8\times10^{-.003431t}+2.1\times10^{-.0869t}+50.1$	[19]
α-d-Xylose	4.4	20.0	+93.6	+18.8	+14,050	----------	$+74.8\times10^{-.0203t}+18.8$	[45]
α-d-Xylose	4.2	0.0	+95.2	+17.3	+14,310	----------	$+77.9\times10^{-.002481t}+17.3$	[45]
α-d-Lyxose	4.0	20.0	+5.6	−13.8	+860	+11,790	$+19.4\times10^{-.0689t}-13.8$	[45]
α-d-Lyxose	3.9	0.2	+4.7	−13.4	+710	+11,340	$+18.1\times10^{-.0686t}-13.4$	----------

β-*d*-Lyxose	4.0	20.0	−72.6	−13.8	−10,930		$-56.8\times10^{-.0001t}-13.8$	[108]
β-*d*-Lyxose	4.0	0.2	−70.8	−13.4	−10,630		$-57.4\times10^{-.0004t}-13.4$	
l-Ribose	4.0	20.0	+20.3	+20.7	+3,050		$-7.6\times10^{-.0492t}+7.2\times10^{-.021t}+20.7$	[109]
l-Ribose	4.1	0.2	+23.4	+23.2	+3,510		$-7.9\times10^{-.0068t}+8.1\times10^{-.004t}+23.2$	[18]
α-*l*-Rhamnose.H_2O	4.0	20.2	−8.6	+8.2	−1,570		$-16.8\times10^{-.0430t}+8.2$	[45, 110]
α-*l*-Rhamnose.H_2O	4.5	0.0	−7.4	+8.7	−1,370		$-16.1\times10^{-.0365t}+8.7$	
α-Lactose.H_2O	7.6	20.0	+85.0	+52.6	+30,620	+18,680	$+32.4\times10^{-.0047t}+52.6$	[105, 45, 111]
α-Lactose.H_2O	4.9	0.2	+86.4	+53.6	+31,130	+18,710	$+32.8\times10^{-.0005t}+53.6$	[71]
β-Lactose	4.0	20.0	+34.9	+55.4	+11,940		$-20.5\times10^{-.0040t}+55.4$	[111, 72]
β-Lactose	3.9	0.2	+36.3	+56.4	+12,420		$-20.1\times10^{-.0005t}+56.4$	[71]
β-Maltose.H_2O	4.2	20.0	+111.7	+130.4	+40,240		$-18.7\times10^{-.0027t}+130.4$	[45]
β-Maltose.H_2O	4.5	0.0	+114.8	+131.5	+41,360		$-16.7\times10^{-.0004t}+131.5$	

[a] [*M*] for 1 molecule of *d*-gulose.

[b] We have prepared this new sugar recently and have included it in order to make this table more complete. Oxidation data are also given in table 7. Additional data concerning this sugar, as well as some of the derivatives of *d*-talose, are now being prepared for publication.

By inspection of table 3 it may be seen that the values of m_1 (the constant representing the principal mutarotation reaction) obtained from the alpha sugars agree within reasonable experimental error with those obtained from the corresponding beta-sugars. The values of m_2 (the constant representing the rapid change) vary over a wider range, but since the experimental error is large the differences are not significant.

The molecular rotations and the differences in the molecular rotations ($2A$) for the alpha and beta isomers are given for convenience in comparing the optical rotations, and to show that the differences in the molecular rotations of the alpha and beta sugars at 0° C are practically the same as those obtained at 20° C.

The initial specific rotation for α-*d*-talose was calculated by Isbell, [39] in 1929 to be +60. This is in approximate agreement with that found (+68). The predicted rotation was based on values for the optical rotations of the various asymmetric carbon atoms, which were calculated by application of the van't Hoff [79, 80] theory of optical superposition. According to the accepted formulas, α-*d*-talose differs from α-*d*-galactose in the configuration of the second carbon, and this difference is analogous to the difference in the structures of α-*d*-mannose and α-*d*-glucose. Sugars which differ in the stereomeric configuration of the second carbon have been designated "epimers" and the difference in their optical rotation is called epimeric difference [38]. According to our measurements at 20° C the difference in the molecular rotations of α-*d*-glucose and α-*d*-mannose is 14,930, and of α-*d*-galactose and α-*d*-talose is 14,900. The approximate agreement might have been anticipated because the two calculations are made on substances which differ only in the configuration of the fourth carbon, and this carbon is removed from the asymmetric center involved in the calculation. The agreement of the optical rotation of talose with the calculated value is probably due in large measure to the similarity of the structures. The new measurements extend the field for such comparison and should aid in the correlation of optical rotation and structure.

The mutarotations of α- and β-*d*-glucose were studied very closely in order to detect any deviations. Reference to table 10, page 179, shows that within experimental error neither alpha nor beta glucose mutarotations deviate from the first-order equation. This is in opposition to the deviations reported by Worley and Andrews. A total of 14 measurements with α- and β-glucose and with α-glucose hydrate were made at 0 and 20° C, and no deviations from the monomolecular equation beyond the experimental error were found. Although the equilibrium specific rotation of *d*-glucose is reported to be independent of the temperature [81] our measurements at 20° C and at 0° C give values of 52.7 and 52.1, respectively. Even though the difference is not large it is sufficient to require revision of the concept that the equilibrium rotation of this sugar is independent of temperature.

The equilibrium rotations of *d*-mannose $CaCl_2.4H_2O$ and *l*-arabinose $CaCl_2.4H_2O$ differ slightly from the equilibrium rotations of the sugars in the absence of calcium chloride. This is due, at least in part, to an alteration in the equilibrium between the various modifications of the sugars by the calcium chloride which is similar to that found by

Isbell for *d*-gulose [82]. By changing the concentration of calcium chloride in aqueous solutions of galactose, arabinose, and mannose, sufficient equilibrium displacements occur to give rise to mutarotation.

As may be seen from the equations in table 3 and the data given on page 180, the mutarotations of both *α*-*d*-gulose $CaCl_2.H_2O$ and (*d*-gulose)$_2$ $CaCl_2.H_2O$ take place in the same direction and at like rates, but the initial rotations (calculated on the same basis) have widely different values. Although the two compounds are crystalline and apparently homogeneous, since the mutarotations follow the monomolecular equation, it seems probable that the compound with lower optical rotation contains some of the heretofore unknown beta modification. The bromine oxidation of *α*-*d*-gulose $CaCl_2.H_2O$ (page 170) proceeds at a fairly uniform rate but that of (*d*-gulose)$_2$ $CaCl_2.H_2O$, table 9, proceeds rapidly until a part of the sugar is used up, and then more slowly as the remaining sugar continues to be oxidized. The rates of reaction indicate that (*d*-gulose)$_2$ $CaCl_2.H_2O$ contains about 32 percent of easily oxidizable sugar. When (*d*-gulose)$_2$ $CaCl_2.H_2O$ was first reported it was thought to represent another ring modification [83] because its optical rotation changed in the same direction as the gulose $CaCl_2.H_2O$, first obtained, while the rate of mutarotation appeared to increase after the first few minutes. Unfortunately the optical rotation was measured in a polariscope tube made of nickel-plated brass. Subsequent investigation has revealed that such tubes give erratic mutarotation measurements. The metal or oxide film appears to dissolve and catalyze the mutarotation reaction. Sugar solutions taken from brass tubes give positive tests for heavy metals with hydrogen sulphide. Although it is recorded in the literature [84] that traces of metals accelerate the rate of mutarotation, this has not been emphasized sufficiently and is not generally appreciated. According to our experience contact of the sugar solutions with nickel, monel metal, brass, and copper causes a drift in the mutarotation constants of the sugars. On the other hand, silver tubes give mutarotation constants which agree with those obtained with glass tubes. The small deviation in the mutarotation of xylose, previously reported by Isbell [85] also appears to be due to experimental error.

The only mutarotations in the group (summarized in table 3) which require two exponential terms for expression are *α*- and *β*-*d*-galactose, *α*- and *β*-*l*-arabinose, *α*-*d*-talose, *d*- and *l*-ribose, and mannose $CaCl_2.4H_2O$. It is possible that there are very small deviations in the mutarotations of some of the others, but careful investigation at 0° C has failed to establish any larger than the experimental error.

In the following table the values of m_1 and m_2 as determined by the various investigators are compared for *α*- and *β*-*d*-galactose and *α*-*l*-arabinose. Where no references are given the values are taken from table 3.

The mutarotations of *α*- and *β*-*d*-galactose are given in figure 4, in which the observed optical rotations are represented by the solid lines; the dotted lines represent the course of a first-order reaction calculated from the constant obtained for the last part of the mutarotation. The distances between the solid and dotted lines represent the deviations. For galactose and arabinose (fig. 4 and 5) the deviations are small; larger differences are found for *α*-*d*-talose (fig. 6) and *l*-ribose (fig. 7).

TABLE 4.—*Comparison of mutarotation constants obtained by different investigators*

Sugar	Temperature	Concentration	m_1	m_2	References
	°C	*Percent*			
α-*d*-Galactose	20.0	5.0	0.00799	0.079	
	20.0	7	.00803	.078	Lowry and Smith [1] [78].
β-*d*-Galactose	20.0	4.0	.00812	.0883	
	20.0	7.7	.00834	.113	Lowry and Smith [78].
	20.0		.0083	.060	Riiber, Minsaas, and Lyche [75].
α-*d*-Galactose	.0	4.1	.00093	.0119	
	.8	10	.00094	.0161	Lowry and Smith [78].
β-*d*-Galactose	.0	4.1	.00090	.0167	
	.8	10	.00094	.0161	Lowry and Smith [78].
α-*l*-Arabinose	20.0	4.3	.030	.138	
	20.0		.029	.108	Riiber and Sørenson [14].

[1] The constants reported by Lowry and Smith were calculated for the natural logarithmic base, but in the above table they have been made comparable to the other values by conversion to the base 10 by use of the factor 0.4343. Since the paper of Lowry and Smith (J. Phys. Chem. **33**, 9 (1929)) is of unusual importance to those applying their method of analysis, it seems desirable to correct a number of obvious typographical errors which might prove confusing. Comparison of the values given in table 4 with those in table 1 (both of their paper) shows that m_1 for the latter table should be 0.00216 instead of 0.000216. In tables 3 and 4 and on page 13, the first terms of the equations representing the mutarotations of the beta forms should be negative. Similarly the values of k_4 at 20° on page 13 should be 0.0788 instead of 0.788; and at 0.8° should be 0.02163 rather than 0.2163.

The reality of the deviations in the mutarotation of *d*-galactose is demonstrated by measuring the optical rotation of a freshly prepared solution containing α- and β-*d*-galactose in the proportions required to give a solution whose optical rotatory power equals the equilibrium rotation. As may be seen by inspection of curve 3 in figure 8 and the data given in table 5, the optical rotation decreases to a minimum at a rate comparable to that of the rapid mutarotation reaction, and thereafter increases at a rate comparable to the slow mutarotation until it reaches the initial value. This complex mutarotation is in marked contrast to the total absence of mutarotation in the case of a similar solution of *d*-glucose [86]. The presence of any mutarotation proves that the equilibrium mixture does not consist solely of the normal alpha and beta isomers.

TABLE 5.—*Mutarotation at 0.3° C of an aqueous solution of α- and β-d-galactose in proportions corresponding to the equilibrium rotation* [1]

$$[°S = 37.91 - 1.15\times10^{-.0016t} + 1.22\times10^{-.0156t}]$$

Time	Observed reading	$m_1\times10^3$	Deviation	$m_2\times10^3$	Time	Observed reading	$m_1\times10^3$	Deviation	$m_2\times10^3$
Minutes	°S				*Minutes*	°S			
3.09	37.84		1.08		61.38	37.05		.13	15.8
4.71	37.78		1.01	18.0	88.4	36.98			
9.19	37.62		0.84	17.9	138.8	37.09	1.08		
12.85	37.55		.76	15.6	180.6	37.16	1.01		
15.49	37.51		.71	14.7	244.8	37.27	1.04		
21.02	37.35		.54	16.8	376.2	37.46	1.10		
25.88	37.27		.44	17.1	∞	37.91			
31.62	37.20		.36	16.7					
43.38	37.07		.20	18.2	Average		1.06		16.8
51.26	37.05		.16	17.2					

[1] The experiment was conducted in a manner analogous to the usual mutarotation measurement, except that a mixture of β-*d*-galactose (2.1334 g) and α-*d*-galactose (0.8975 g) was used. The solution, made by adding approximately 75 ml of water to this mixture, was read in a 4-dm tube.

Another method for the study of the complex mutarotation reactions was outlined in a previous publication [19] in which we called attention to the surprisingly large differences in the equilibrium rotations of gal-

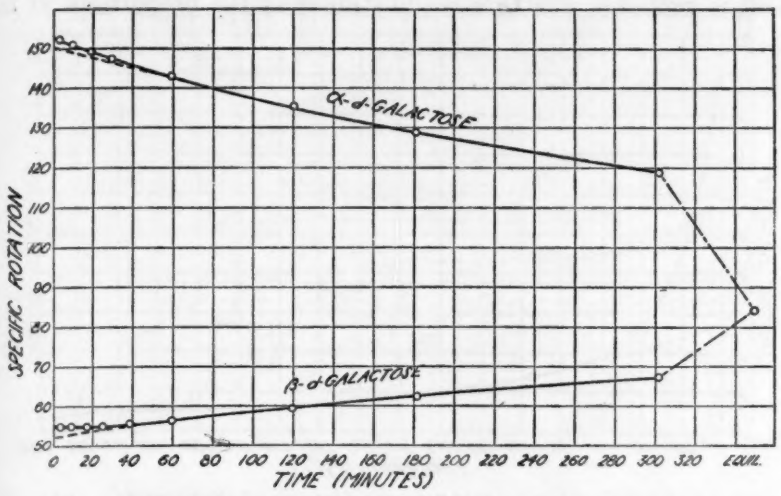


FIGURE 4.—*Mutarotation of α- and β-d-galactose in water at* 0° C.

actose, arabinose, and talose at various temperatures and showed that after changing the temperature complex "thermal mutarotations" occur. As may be seen from curve *II* in figure 8, the optical rotation of an aqueous solution of *d*-galactose after lowering the temperature

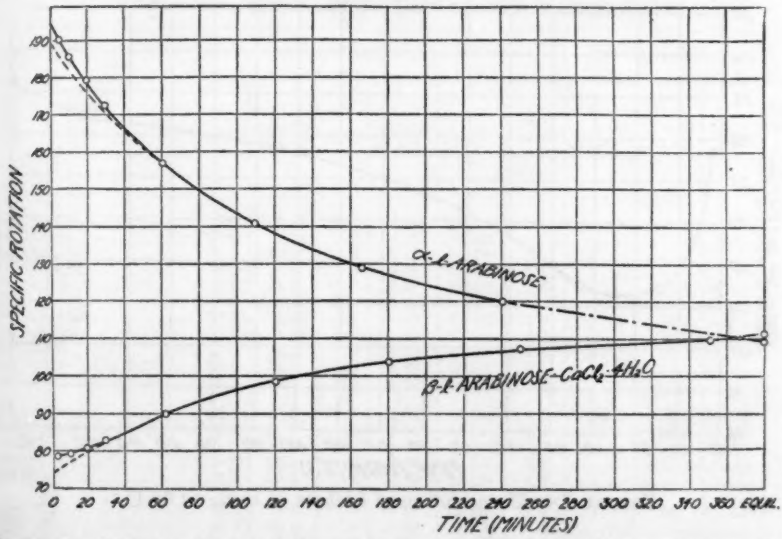


FIGURE 5.—*Mutarotations of α-l-arabinose and β-l-arabinose* $CaCl_2.4H_2O$ *in water at* 0° C.

from 25 to 0° C rises to a maximum and then decreases. Analysis of the data and the development of equations similar to those used for the mutarotations of the crystalline sugars show that the thermal mutarotation consists in two reactions. The first is rapid and appears

to take place at the same rate as the rapid reaction found in the mutarotations of α- and β-*d*-galactose. A large part of the thermal mutarotation is due to this rapid reaction; the subsequent slow reaction, which is probably due to a readjustment in the proportions of the

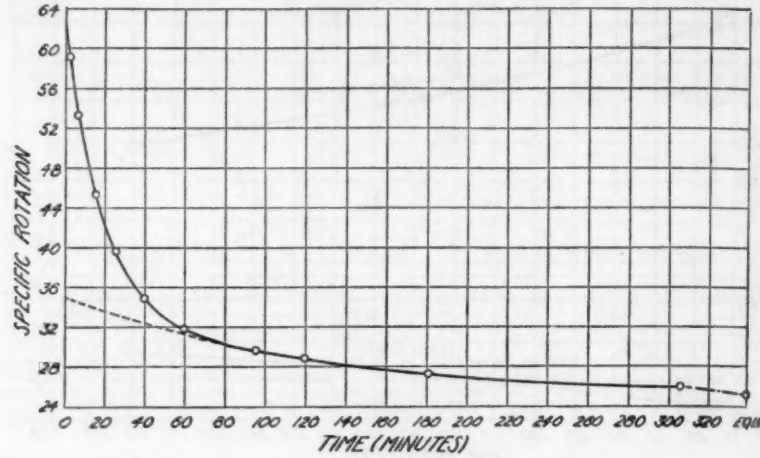


FIGURE 6.—*Mutarotation of α-d-talose in water at* 0° C.

normal alpha and beta isomers, causes only a small change in optical rotation. As might be expected, the thermal mutarotation of arabinose (curve *I*) is similar to that of galactose. The thermal mutarotation of talose consists in a rapid change which is followed by a small but

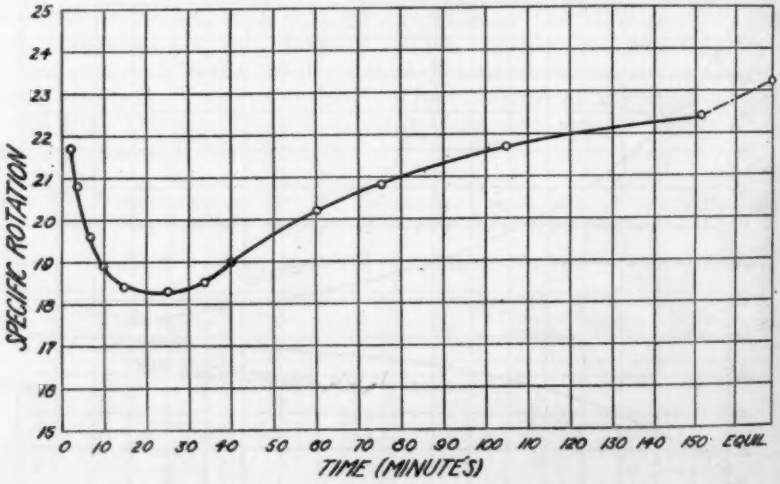


FIGURE 7.—*Mutarotation of l-ribose in water at* 0° C.

real slow change. The data on the thermal mutarotations are given in detail in table 12.

The variation of the equilibrium proportions of the labile constituents with temperature, as revealed by the thermal mutarotations, indicates that the heat of the rapid reaction is considerable and probably larger than the heat of reaction for the slow change. Information

with respect to the heat of activation, Q, can be derived from a comparison of the velocity constants at different temperatures. The results of such comparison are given in table 6.

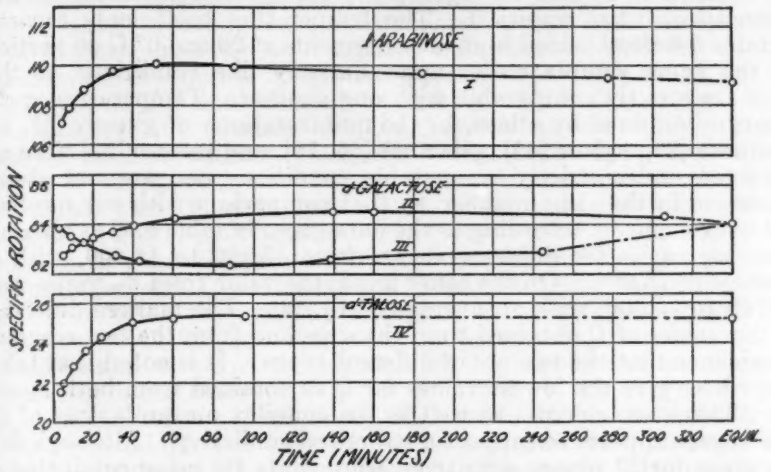


FIGURE 8.—*New methods for demonstrating complex character of equilibrium solutions*

Curve *I.* Thermal mutarotation of *l*-arabinose at 0° C.

Curve *II.* Thermal mutarotation of *d*- galactose at 0° C.

Curve *III.* Mutarotation at 0.3° C of an aqueous solution of α- and β-*d*-galactose in proportions corresponding to the equilibrium rotation.

Curve *IV.* Thermal mutarotation of *d*-talose at 0° C.

TABLE 6.—*Effect of temperature on rates of mutarotation*

Sugar	Slow change						Rapid change			
	t_1°C	$m_1\times10^3$ at t_1° C	t_2°C	$m_2\times10^3$ at t_2°C	Q	Temperature coefficient [1]	$m_2\times10^3$ at t_1°C	$m_2\times10^3$ at t_2°C	Q	Temperature coefficient [1]
α-*d*-Glucose	20.0	6.32	0.2	0.741	17,200	2.6				
β-*d*-Glucose	20.0	6.25	.2	.738	17,200	2.6				
α-*d*-Mannose	20.0	17.3	.2	2.16	16,700	2.5				
β-*d*-Mannose	20.0	17.8	.3	2.14	17,100	2.5				
Mannose $CaCl_2.4H_2O$	20.0	24.5	.0	2.67	17,600	2.6	311	60.8	13,000	2.0
α-*d*-Galactose	20.0	8.03	.0	.93	17,100	2.5	79.0	11.9	15,000	2.3
β-*d*-Galactose	20.0	8.12	.0	.90	17,500	2.6	88.3	16.7	13,200	2.1
α-*d*-Talose	20.0	26.3	.1	3.62	15,900	2.4	126	25.5	12,800	2.0
α-*d*-Gulose $CaCl_2.H_2O$	20.0	19.1	.2	1.88	18,600	2.8				
(*d*-Gulose)$_2$ $CaCl_2.H_2O$	20.1	19.7	.2	2.02	18,200	2.7				
α-*l*-Arabinose	20.0	30.0	.0	3.62	16,800	2.5	138	21.7	14,700	2.2
β-*l*-Arabinose $CaCl_2.4H_2O$	20.0	30.0	.0	3.84	16,300	2.4	169	36.9	12,100	1.9
α-*d*-Lyxose	20.0	56.8	.2	8.44	15,300	2.3				
β-*d*-Lyxose	20.0	59.1	.2	8.40	15,700	2.4				
α-*d*-Xylose	20.0	20.3	.0	2.45	16,800	2.5				
l-Ribose	20.0	49.2	.2	6.87	15,800	2.4	231	54	11,700	1.9
α-*l*-Rhamnose.H_2O	20.2	43.0	.0	5.68	15,900	2.4				
α-Lactose.H_2O	20.0	4.71	.2	.544	17,300	2.6				
β-Lactose	20.0	4.66	.2	.524	17,600	2.6				
β-Maltose.H_2O	20.0	5.27	.0	.580	17,500	2.6				
Average					16,900	2.52			13,200	2.06

[1] $\frac{m \text{ at } 35°\text{ C}}{m \text{ at } 25°\text{ C}}$ as calculated from the value of Q by use of the equation $\log \frac{m \text{ at } 35°}{m \text{ at } 25°} = \frac{Q}{42,111}$.

Inasmuch as m_1 and m_2 are not necessarily true velocity constants but probably represent complex changes, Q as obtained by the Arrhenius equation does not correspond to the activation of any one substance but applies to a group of substances and should be considered somewhat empirical. The temperature coefficients reported in table 6 were obtained from measurements at 20 and 0° C on portions of the same sample under approximately like conditions, so that they are strictly comparable with one another. Temperature coefficients determined by others for the mutarotations of glucose [67, 88], mannose [89], xylose [45], galactose [66, 78], and lactose [27] were not obtained under strictly comparable conditions and are not always expressed in the same manner, so that comparison with our results is not convenient. According to the data given in table 6, Q as obtained from m_1 varies for different sugars from 15,300 to 18,600, with an average of 16,900. On the other hand, the value from m_2 varies from 11,700 to 15,000, with an average of 13,200. The marked difference in the values of Q obtained from the slow and from the fast reactions is evidence that the two are of different types. It is noted that talose and ribose give the lowest values for Q as obtained from both m_1 and m_2. This characteristic as well as the complex mutarotations of the two sugars appears to support a structural similarity. Although data are given for 20 sugars, similar measurements are being conducted on the remaining sugars because a complete study may reveal important differences and correlations which are not apparent from the study of only a few individuals.

IV. EXPERIMENTAL PROCEDURE

1. PREPARATION AND PURIFICATION OF THE SUGARS

The numerous errors in the optical rotations recorded in the literature attest to the need of great care in the preparation and purification of the sugars used for physical measurements. The tendency of two or more forms of the same sugar to crystallize simultaneously always leaves some uncertainty as to the homogeneity of the product, and it is only after many crystallizations under widely different conditions that it may be assumed that the product is pure. Because pure products are obtained only by slow crystallizations, whenever possible the sugars used in this investigation were crystallized very slowly in the following manner: A slightly supersaturated solution of the sugar was prepared, seeded with the desired modification and placed in a flask, which was rotated slowly for at least 1 week while crystallization took place. The crystals were then separated, washed thoroughly with aqueous alcohol, and dried at 50° C in vacuo. The samples of *α-d*-glucose, mannose $CaCl_2.4H_2O$, *α-d*-galactose, *α-d*-talose, *α-d*-gulose $CaCl_2.H_2O$, *α-l*-arabinose, *α-d*-xylose, *α-l*-rhamnose hydrate, lactose hydrate, and maltose hydrate were crystallized in this manner from aqueous solution; *α-* and *β-d*-lyxose, *α-d*-mannose, and *d-* and *l*-ribose were crystallized slowly from aqueous methyl or ethyl alcohol, while *β-d*-mannose was crystallized in like manner from acetic acid. The crystallizations of *β-d*-glucose and *β-d*-galactose were carried out rapidly from aqueous acetic acid according to the method of Hudson and Dale [90]. Although two forms of *l*-arabinose are known, only

one exists as the free crystalline sugar. The other modification is available as a calcium chloride compound which was prepared by Dale [91] and also, independently at about the same time, by Austin and Walsh [92], who kindly supplied us with some of their product for use in the present investigation. As explained on page 145, the crystalline form of *l*-arabinose (+191) is called *α-l*-arabinose, and the calcium chloride modification is designated *β-l*-arabinose $CaCl_2.4H_2O$, in contradiction to the nomenclature of Austin and Walsh as well as of Montgomery and Hudson [93]. Inasmuch as the initial specific rotation of *β-l*-arabinose $CaCl_2.4H_2O$ was reported by Austin and Walsh to correspond to +75 for the arabinose constituent, while Montgomery and Hudson gave +89.4, we prepared a new sample and determined the specific rotation. It gives $[\alpha]_D^{20}=+34.7$, which corresponds to a specific rotation of +77 for the arabinose constituent. In our experience *β-l*-arabinose $CaCl_2.4H_2O$ on recrystallization loses calcium chloride very readily and gives a mixture containing $(\alpha\text{-}l\text{-arabinose})_2CaCl_2.2H_2O$. This can be avoided by conducting the crystallization at a low temperature in the presence of an excess of calcium chloride.

The sample of $(d\text{-gulose})_2\ CaCl_2.H_2O$ used in this investigation was obtained by adding hot ethyl alcohol to a concentrated aqueous solution of *α-d*-gulose $CaCl_2.H_2O$. By crystallization in this manner the original double compound gives up half of its calcium chloride.[3] The resulting crude product was recrystallized by dissolving it in a small quantity of water, adding several volumes of ethyl alcohol, and allowing crystallization to proceed slowly over the course of about 1 week.

The sample of *α-d*-talose was prepared from *d*-galactose by the method of Levene and Tipson [94]. The crude sugar was recrystallized from aqueous alcohol until further recrystallization did not lower the equilibrium rotation. It was then recrystallized very slowly from water.

The samples of *α*- and *β-d*-lyxose were prepared from calcium galactonate by the method of Ruff and Ollendorf [95] as modified by Hockett and Hudson [96]. The crystalline sugars were separated originally from aqueous alcoholic solutions without the use of seed crystals. Particular care must be used in the crystallization of the alpha form to avoid accidental seeding with the beta form. The recrystallizations were conducted slowly from aqueous methyl alcohol in the usual manner.

2. BROMINE OXIDATION MEASUREMENTS

In conducting the oxidation measurements the crystalline sugar (0.025 mole) or the equilibrium solution (0.025 mole of sugar in 100 ml of water) was added to a cold mixture consisting of 10 ml of bromine, 30 g of barium carbonate, and either 500 ml or 400 ml of aqueous barium bromide solution containing 30 g of $BaBr_2.2H_2O$ and saturated with carbon dioxide. The oxidation mixture was contained in a 1-liter 3-neck flask which was surrounded with a cooling bath and equipped with a mechanical stirrer and a thermocouple for measuring the temperature. A slow stream of carbon dioxide saturated with bro-

[3] According to a private communication from J. K. Dale, *d*-glucose $CaCl_2$ also loses $CaCl_2$ by crystallization from ethyl alcohol and gives a product which appears to be similar to $(d\text{-gulose})_2\ CaCl_2.H_2O$.

mine vapor was bubbled through the flask during the reaction. The concentration of bromine was determined at various times by sodium thiosulphate titration of the iodine liberated from potassium iodide by a weighed sample of the mixture. The concentration of the sugar was measured at intervals on samples in which the oxidation had been stopped by the removal of the bromine with linseed oil solution (1 part of raw oil dissolved in 2 parts of benzene). Sugar was determined in the filtered solutions by Scales' method [97], slightly modified by increasing the time of boiling to 6 minutes and increasing the time required to produce boiling to 4 minutes. The procedure was standardized by determinations on known quantities of the sugar in the presence of various concentrations of barium bromide. In calculating the results, allowance was made for the increase in volume caused by reaction of the barium carbonate with hydrobromic acid to produce barium bromide. This was determined by measuring the change in volume caused by adding known quantities of barium bromide to glucose solutions. The initial increase of volume resulting from the addition of the crystalline sugar was also measured and taken into account.

It was shown previously [4] that the oxidant is free bromine and that the oxidation can be represented by the equation in which a is the

$$ak=\frac{1}{t}\log\frac{A}{A-X}, \tag{7}$$

concentration of free bromine, while A and $A-X$ are the quantities of the unoxidized sugar at the beginning and end of the time interval, t. The concentrations of free bromine were read from a chart based on results obtained from the following equation, which was developed in a previous article [4]:

$$Br^3_2+(0.482+2B-C)Br^2_2+[0.0246+0.482(B-C)]Br_2-0.0246C=0, \tag{8}$$

in which Br_2 is the concentration of free bromine, B is the average bromide, and C is the average bromine concentration. The average bromide content for each oxidation period is calculated from the mean amounts of bromide present by multiplying each mean by the time interval for which it is the average and dividing the sum of the products by the total time covered. The average bromine content and the temperature were averaged in like manner. The oxidations of the various crystalline sugars are outlined in table 7, while a summary of the results is given in table 1, page 146. In general, the values of k were as uniform as could be expected for measurements of this type. In a few cases, notably for α-*d*-galactose, α-*d*-xylose, α-*d*-mannose, and *d*-gulose $CaCl_2.H_2O$ the value of k appears to decrease as the reaction proceeds. This may be caused by the accumulation of less readily oxidizable material in solution or by the production of by-products which are capable of reducing the alkaline copper reagent used in determining the unoxidized sugar.

TABLE 7.—*Bromine oxidation of freshly dissolved crystalline sugars*

Time after beginning oxidation	Unoxidized sugar	Oxidation	Averages for oxidation period				Velocity constants $ak=\frac{1}{t}\log\frac{A}{A-X}$	
			Temperature	Bromide Br^-	Bromine Br_2	Free bromine a	$ak\times10^3$	$k\times10^3$
α-d-GLUCOSE								
Minutes	g	*Percent*	°C	*Moles/liter*	*Moles/liter*	*Moles/liter*		
1.4	4.59	0						
5.1	4.47	2.6	+0.3	0.360	0.368	0.089	3.11	34.9
30.0	3.83	16.6	+.2	.367	.372	.088	2.75	31.3
60.1	3.27	28.8	+.2	.374	.374	.086	2.51	29.2
120.0	2.335	49.1	+.4	.386	.375	.084	2.47	29.4
180.2	1.640	64.3	+.3	.396	.374	.081	2.50	30.9
240.0	1.190	74.1	+.5	.403	.373	.078	2.46	31.5
300.2	.565	87.7	+.5	.411	.375	.077	3.04	39.5
Average			+.3	.385	.373	.083	2.69	32.4
β-d-GLUCOSE								
0	(4.756)	0						
1.3	3.495	26.5	+0.5	0.369	0.358	0.082		
3.3	2.330	51.0		.384	.355	.078	88.0	1,128
5.1	1.655	65.2	+.3	.394	.352	.074	85.4	1,154
8.3	.837	82.4		.408	.346	.069	88.7	1,286
11.1	.483	89.8	.0	.417	.341	.065	87.7	1,349
15.5	.204	95.7		.426	.340	.064	86.9	1,358
25.3	.080	98.3	−.2	.437	.340	.062	(68.3)	(1,102)
Average			+.2	.405	.347	.071	87.3	1,255
α-d-GALACTOSE								
2.8	4.570	0	(+0.47)					
6.8	4.355	4.7	+.51	0.360	0.384	0.095	5.19	54.6
16.2	4.020	11.9	+.64	.365	.383	.091	4.16	45.7
29.9	3.590	21.3	+.57	.371	.381	.090	3.87	43.0
59.8	2.883	36.9	+.44	.375	.379	.088	3.51	39.9
90.4	2.380	47.9	+.41	.387	.377	.084	3.23	38.5
119.8	1.985	56.6	+.38	.396	.376	.081	3.10	38.3
179.6	1.440	68.5	+.34	.405	.374	.078	2.84	36.4
Average			+.47	.376	.379	.087	3.70	42.3
β-d-GALACTOSE								
0	(4.895)	0	(+0.12)					
0.7	4.008	18.1	+.30	0.363	0.350	0.078		
2.1	2.790	43.0	+.54	.376	.347	.076	112.4	1,479
4.0	1.748	64.3	+.72	.391	.344	.072	109.2	1,517
6.9	.848	82.7	+.80	.407	.342	.068	108.9	1,600
10.1	.379	92.3	+.79	.419	.340	.065	109.0	1,677
15.0	.116	97.6	+.70	.430	.338	.063	107.6	1,708
20.1	.057	98.8	+.60	.435	.337	.061	95.2	1,561
30.2	.041	99.2					(67.4)	
Average			+.64	.403	.343	.069	107.0	1,590
α-d-MANNOSE								
1.5	4.473	0	(+0.14)					
5.0	4.300	3.9	+.15	0.360	0.366	0.088	4.89	55.6
30.1	3.258	27.2	+.14	.373	.364	.083	4.81	58.0
59.9	2.491	44.3	+.14	.384	.364	.080	4.35	54.4
120.0	1.591	64.4	+.15	.398	.362	.076	3.79	49.9
179.8	1.063	76.2	+.14	.409	.361	.073	3.50	47.9
240.0	.737	83.5	+.14	.416	.361	.072	3.28	45.6
300.2	.519	88.4	+.15	.422	.361	.068	3.13	46.0
Average			+.14	.395	.363	.077	3.96	51.1

TABLE 7.—*Bromine oxidation of freshly dissolved crystalline sugars*—Continued

Time after beginning oxidation	Unoxidized sugar	Oxidation	Averages for oxidation period				Velocity constants $ak=\frac{1}{i}\log\frac{A}{A-X}$	
			Temperature	Bromide Br^-	Bromine Br_2	Free bromine a	$ak\times10^3$	$k\times10^3$
β-d-MANNOSE								
Minutes	g	*Percent*	°C	*Moles/liter*	*Moles/liter*	*Moles/liter*		
0	(4.625)	0	(+0.20)					
1.2	3.850	16.8	+.46	0.366	0.363	0.085		
2.4	3.257	29.6	+.59	.373	.362	.083	60.5	729
3.8	2.680	42.1	+.65	.380	.360	.080	60.5	756
6.8	1.777	61.6	+.66	.392	.356	.076	60.0	789
9.9	1.206	73.9	+.63	.402	.353	.072	57.9	804
14.9	.656	85.8	+.45	.414	.349	.068	56.1	825
29.9	.218	95.3	+.36	.431	.344	.064	(43.4)	(678)
Average			+.54	.394	.355	.075	59.0	781
α-d-TALOSE								
0.9	4.650	0	(+0.19)					
4.2	4.440	4.5	+.22	0.361	0.388	0.096	(6.08)	(63.3)
15.0	3.777	18.8	+.23	.368	.385	.092	6.46	70.2
29.9	2.891	37.8	+.23	.378	.383	.089	7.12	80.0
60.2	1.822	60.8	+.21	.393	.384	.084	6.86	81.7
90.0	1.172	74.8	+.20	.404	.384	.082	6.72	82.0
150.2	.535	88.5	+.19	.418	.389	.080	6.29	78.6
210.7	.295	93.7	+.18	.428	.399	.081	5.71	(70.5)
Average			+.21	.393	.387	.085	6.69	78.5
β-d-TALOSE								
0	0.180	0	(+0.5)					
1.1	.1585	11.9		0.364	0.362	0.083	50.3	607
10.0	.0517	71.3		.393	.333	.068	54.2	797
Average			(+.5)	.378	.348	.076	52.3	702
α-d-GULOSE $CaCl_2$. H_2O								
0.8	4.313	0						
5.1	3.987	7.6	+0.32	0.365	0.394	0.097	7.94	81.9
15.2	3.560	17.5	+.32	.375	.371	.086	5.79	67.3
30.0	2.861	33.7	+.30	.384	.346	.077	6.10	79.2
60.7	2.047	52.5	+.30	.394	.348	.073	5.40	74.0
123.4	1.133	73.7	+.28	.409	.350	.068	4.74	69.7
180.1	0.730	83.1	+.26	.418	.346	.064	4.30	67.2
305.8	.359	91.7		.429	.350	.063	3.54	56.2
Average			.30	.396	.358	.075	5.43	70.8
α-LACTOSE								
4.9	8.800	0	(+0.15)					
30.3	7.540	14.3	+.17	0.372	0.364	0.084	2.64	31.4
61.6	6.280	28.6	+.17	.380	.361	.080	2.58	32.3
119.9	4.820	45.2	+.17	.390	.358	.077	2.27	29.5
180.1	3.780	57.0	+.16	.398	.354	.074	2.09	28.2
239.9	3.055	62.3	+.15	.404	.351	.071	1.96	27.6
300.0	2.480	71.8	+.14	.409	.348	.069	1.86	27.0
Average			+0.16	0.392	0.356	0.076	2.23	29.3

TABLE 7.—*Bromine oxidation of freshly dissolved crystalline sugars*—Continued

Time after beginning oxidation	Unoxidized sugar	Oxidation	Averages for oxidation period				Velocity constants $ak=\frac{1}{t}\log\frac{A}{A-X}$	
			Temperature	Bromide Br^-	Bromine Br_2	Free bromine a	$ak\times10^3$	$k\times10^3$
β-LACTOSE								
Minutes	g	*Percent*	°C	*Moles/liter*	*Moles/liter*	*Moles/liter*		
0	(9.978)	0						
1.2	7.833	21.5	+0.19	0.363	0.379	0.092		
2.3	6.503	34.8	+.34	.368	.376	.089	73.5	826
4.1	4.216	57.7	+.47	.380	.372	.084	92.8	1,105
7.0	2.928	70.7	+.52	.396	.369	.079	73.7	933
10.0	1.811	81.9	+.51	.406	.366	.075	72.3	964
13.1	1.109	88.9	+.45	.414	.364	.073	71.3	977
20.0	0.502	95.0	+.37	.426	.362	.070	63.5	907
30.2	.330	96.7	(+.27)	(.435)	(.361)	(.068)	(47.4)	(697)
Average			+.46	.404	.367	.076	74.6	952
β-MALTOSE								
0	(10.488)	0						
1.2	7.060	32.7	+0.44	0.369	0.359	0.083		
3.3	4.493	57.2	+.69	.385	.356	.077	(178.4)	(2,317)
5.6	2.717	74.1	+.82	.399	.352	.073	94.3	1,292
8.8	1.358	87.1	+.82	.412	.349	.071	94.2	1,327
14.7	.469	95.5	+.68	.427	.345	.067	131.6	1,964
30.0	.231	97.8	+.48	.441	.342	.059	(168.5)	(2,856)
Average			+0.65	0.405	0.350	0.072	106.7	1,528
α-*l*-RHAMNOSE								
1.0	4.625	0	(+0.10)					
5.1	4.270	7.7	+.14	0.362	0.365	0.086	8.45	98.3
31.3	2.705	41.5	+.16	.381	.365	.081	7.69	94.9
65.3	1.625	64.9	+.16	.397	.350	.075	7.06	94.1
120.1	.838	81.9	+.16	.413	.344	.067	6.23	93.0
183.8	.437	90.6	+.16	.424	.341	.064	5.61	87.7
240.2	.265	94.3	+.16	.430	.340	.063	5.19	82.4
300.2	.179	96.1	+.16	.435	.338	.061	4.72	77.4
Average			+.16	.406	.349	.071	6.42	89.7
α-*l*-ARABINOSE								
1.0	3.862	0	(+0.09)					
2.0	3.792	1.8	+.11	0.359	0.363	0.087	7.94	91.3
4.2	3.648	5.5	+.16	.361	.362	.086	7.74	90.0
8.1	3.397	12.0	+.23	.364	.361	.085	7.85	92.4
12.2	3.127	19.0	+.25	.368	.361	.083	8.19	98.7
19.9	2.740	29.1	+.31	.374	.359	.081	7.89	97.4
50.1	1.660	57.0	+.26	.390	.356	.076	7.47	98.3
80.0	1.084	72.4	+.26	.403	.354	.072	7.09	98.5
119.9	0.610	84.2	+.27	.414	.351	.069	6.74	97.7
180.0	.295	92.4	+.27	.425	.349	.067	6.24	93.1
Average			+.23	.384	.357	.078	7.46	95.3
β-*l*-ARABINOSE $CaCl_2.4H_2O$								
0	(3.956)	0						
0.8	3.070	22.4	+0.31	0.367	0.359	0.083		
2.1	2.166	45.2	+.51	.380	.356	.078	116.5	1,494
3.9	1.298	67.2	+.62	.395	.354	.074	120.6	1,630
6.8	.586	85.2	+.66	.411	.352	.070	119.9	1,713
12.9	.119	97.0	+.57	.429	.347	.065	116.7	1,795
Average			+.53	.396	.354	.074	118.4	1,658

TABLE 7.—*Bromine oxidation of freshly dissolved crystalline sugars*—Continued

Time after beginning oxidation	Unoxidized sugar	Oxidation	Averages for oxidation period				Velocity constants $ak=\frac{1}{t}\log\frac{A}{A-X}$	
			Temperature	Bromide Br^-	Bromine Br_2	Free bromine a	$ak\times10^3$	$k\times10^3$
α-*d*-XYLOSE								
Minutes	*g*	*Percent*	°C	*Moles/liter*	*Moles/liter*	*Moles/liter*		
1.2	3.740	0	(+0.20)					
5.0	3.480	7.0	+.26	0.360	0.357	0.084	8.23	98.0
30.1	2.140	42.8	+.30	.374	.353	.078	8.39	107.6
60.0	1.410	62.3	+.30	.395	.350	.073	7.20	98.6
120.3	.704	81.2	+.28	.412	.346	.067	6.09	90.9
182.3	.391	89.5	+.26	.423	.344	.065	5.42	83.4
240.3	.258	93.1	+.25	.430	.343	.064	4.86	75.9
300.0	.144	96.1	+.24	.434	.343	.063	4.73	75.1
Average			+.27	.404	.348	.071	6.42	89.9
CRYSTALLINE *d*-RIBOSE								
0.9	3.641	0	(+0.17)					
1.8	3.357	7.8	+.22	0.363	0.373	0.089	(39.2)	
7.3	2.742	24.7	+.31	.368	.368	.086	19.2	223
29.8	1.245	65.8	+.29	.397	.359	.075	16.1	215
60.3	.554	84.8	+.27	.416	.353	.069	13.8	200
120.2	.139	96.2	+.25	.431	.347	.065	11.9	183
209.4	.033	99.1	+.24	.441	.345	.062	9.8	158
Average			+.26	.403	.358	.074	14.2	196
CRYSTALLINE *l*-RIBOSE								
0.8	3.760	0	(+0.16)					
2.9	3.420	9.0	+.22	0.362	0.390	0.097	19.6	202
6.9	2.830	24.7	+.26	.369	.386	.092	20.2	220
14.8	2.090	44.4	+.27	.382	.383	.087	18.2	209
30.0	1.226	67.4	+.24	.398	.378	.081	16.7	206
45.2	.785	79.1	+.21	.409	.375	.077	15.2	197
60.0	.522	86.1	+.20	.417	.374	.075	14.5	193
180.2	.054	98.6	+.15	.439	.371	.070	10.3	147
Average			+.22	.397	.380	.083	16.4	195
α-*d*-LYXOSE								
1.1	3.734	0	(+0.20)					
5.0	3.317	11.2	+.26	0.363	0.390	(0.096)	(13.2)	(138)
15.2	2.376	26.4	+.28	.377	.386	.090	13.9	154
30.1	1.520	59.3	+.26	.391	.382	.084	13.5	161
60.2	.699	81.3	+.20	.410	.377	.078	12.3	158
90.2	.348	90.7	+.18	.421	.375	.075	11.6	155
120.2	.175	95.3	+.17	.429	.375	.073	11.2	153
180.4	.061	98.4	+.16	.438	.376	(.072)	10.0	(139)
Average			+.22	.404	.380	.080	12.3	156
β-*d*-LYXOSE								
0	(3.808)	0						
0.8	3.543	7.0	+0.20			0.087		
3.1	2.882	24.3	+.30	0.373	0.376	.087	39.0	448
5.7	2.320	39.1	+.37	.381	.373	.084	37.5	446
9.0	1.782	53.2	+.45	.390	.364	.079	36.4	461
13.1	1.345	64.7	+.45	.399	.358	.075	34.2	456
20.0	.893	76.5	+.44	.409	.354	.072	31.2	433
30.4	.594	84.4	+.44	.419	.349	(.067)	(26.2)	(391)
Average			+.38	.395	.362	.079	35.7	449

In order to measure the rates for the oxidation of the equilibrium solutions the required quantity of sugar was dissolved in 100 ml of water and allowed to stand at 0° C until equilibrium was established, after which the solution was added to the oxidation mixture in place of the crystalline sugar. Samples of the reacting mixture were taken and analyzed, as previously described.

TABLE 8.—*Bromine oxidations of aqueous sugar solutions in equilibrium at the beginning of the oxidation*

Time	Temperature	Averages for the oxidation period			Unoxidized sugar			Oxidized sugar	Velocity constants			
		Bromide (Br^-)	Bromine (Br_2)	Free bromine (a)	Total	More reactive fraction	Less reactive fraction		More reactive fraction		Less reactive faction	
									$ak_B \times 10^3$	$k_B \times 10^3$	$ak_A \times 10^3$	$k_A \times 10^3$
1	2	3	4	5	6	7	8	9	10	11	12	13
					d-GLUCOSE							
Minutes	°C	*Moles/liter*	*Moles/liter*	*Moles/liter*	g	g	g	*Percent*				
0	+0.6	------	------	------	(4.727)	2.960	1.767	0.0	------	------	------	------
1.3	+.6	0.365	0.346	0.079	3.900	2.145	1.755	17.5	------	------	------	------
4.8	+.6	.379	.344	.075	2.740	1.013	1.727	43.0	93.1	1,241	------	------
9.7	+.5	.393	.342	.071	1.990	.299	1.691	57.1	101.9	1,435	------	------
15.0	+.4	.402	.340	.068	1.760	.104	1.656	62.8	95.9	1,410	------	------
30.2	+.4	.412	.338	.065	1.560	------	1.560	66.0	------	------	------	------
122.4	+.4	.425	.334	.062	1.055	------	1.055	77.7	------	------	1.84	29.7
239.9	+.4	.432	.330	.060	.710	------	.710	85.0	------	------	1.63	27.2
329.9	+.4	.436	.326	.058	.560	------	.560	88.2	------	------	1.48	25.5
Average	+.48	.406	.337	.067	------	------	------	------	------	1,362	------	27.5
					d-MANNOSE							
0	(+0.10)	------	------	------	(4.634)	1.440	3.194	0.0	------	------	------	------
0.9	+.24	0.360	0.372	0.090	4.395	1.227	3.168	5.1	------	------	------	------
3.9	+.29	.366	.372	.087	3.806	.722	3.084	17.9	76.8	883	------	------
7.9	+.30	.372	.372	.085	3.352	.373	2.979	27.7	73.9	869	------	------
15.0	+.30	.380	.372	.082	2.946	.136	2.810	36.4	67.8	827	------	------
30.2	+.27	.389	.372	.078	2.499	------	2.499	46.1	------	------	------	------
55.9	+.19	.398	.372	.075	2.017	------	2.017	56.5	------	------	3.62	48.3
119.9	+.17	.410	.372	.071	1.274	------	1.274	72.5	------	------	3.26	45.9
179.9	+.16	.418	------	.069	.876	------	.876	81.1	------	------	3.04	44.1
243.4	+.18	.425	------	.068	.609	------	.609	86.9	------	------	2.88	42.4
359.7	+.19	.432	------	.067	.355	------	.355	92.3	------	------	(2.57)	(38.4)
Average	+.23	.395	.372	.077	------	------	------	------	------	860	------	45.2
					d-GALACTOSE IN EQUILIBRIUM AT 0° C							
0	(+0.19)	------	------	------	(4.782)	3.280	1.502	0.0	------	------	------	------
1.4	+.49	0.368	0.359	0.083	3.557	2.070	1.487	25.6	------	------	------	------
4.8	+.83	.387	.357	.077	2.210	.755	1.455	53.8	128.8	1,673	------	------
10.1	+.55	.399	.354	.073	1.561	.152	1.409	67.4	130.4	1,786	------	------
15.1	+.36	.408	.352	.071	1.414	.046	1.368	70.4	120.7	1,700	------	------
25.7	+.21	.417	.349	.068	1.282	------	1.282	73.2	------	------	------	------
40.0	+.22	.422	.348	.067	1.178	------	1.178	75.4	------	------	2.76	41.2
70.2	+.22	.427	.346	.065	.990	------	.990	79.3	------	------	2.58	39.7
152.2	+.20	.433	.347	.062	.650	------	.650	86.4	------	------	2.35	37.9
275.0	+.18	.440	.348	.062	.405	------	.405	91.5	------	------	2.02	32.6
400.0	+.20	.443	.349	.062	.330	------	.330	93.1	------	------	1.58	(25.5)
Average	+.35	.414	.351	.069	------	------	------	------	------	1,720	------	37.9

TABLE 8.—*Bromine oxidations of aqueous sugar solutions in equilibrium at the beginning of the oxidation*—Continued

Time	Temperature	Averages for the oxidation period			Unoxidized sugar			Oxidized sugar	Velocity constants			
									More reactive fraction		Less reactive faction	
		Bromide (Br^-)	Bromine (Br_2)	Free bromine (a)	Total	More reactive fraction	Less reactive fraction		$ak_B\times10^3$	$k_B\times10^3$	$ak_A\times10^3$	$k_A\times10^3$
1	2	3	4	5	6	7	8	9	10	11	12	13
					d-GALACTOSE IN EQUILIBRIUM AT 20° C							
0	(−1.09)				(4.521)	3.069	1.452	0.0				
1.1	+.85	0.368	0.350	0.079	3.590	2.148	1.442	20.6				
4.9	+.12	.388	.349	.074	2.169	.760	1.409	52.0	118.7	1,604		
15.0	+.24	.409	.345	.068	1.366	.030	1.336	69.8	133.4	1,962		
25.7	+.15	.417	.343	.066	1.264		1.264	72.0				
40.1	+.14	.422	.341	.065	1.558		1.158	74.4			2.64	40.6
80.4	+.14	.429	.343	.064	.924		.924	79.6			2.49	38.9
127.7	+.15	.433	.345	.064	.736		.736	83.7			2.30	35.9
193.1	+.17	.437	.352	.065	.557		.557	87.7			2.13	32.8
240.2	+.15	.439	.350	.069	.466		.466	89.7			2.02	29.3
360.2	+.11	.442	.374	.070	.346		.346	92.3			(1.68)	(24.0)
Average	+.22	.418	.350	.068						1,783		35.5
					(*d*-GULOSE)$_3$ $CaCl_2.H_2O$							
0	(+0.12)				(4.732)	3.855	0.877					
0.8	+.34	0.358	0.368	0.089	4.470	3.600	.870	5.5				
4.9	+.53	.368	.365	.085	3.440	2.606	.834	27.3	34.2	402		
14.8	+.43	.387	.360	.078	2.015	1.252	.763	57.4	32.8	421		
29.9	+.37	.405	.354	.072	1.126	.450	.676	76.2	31.0	431		
59.8	+.30	.423	.348	.066	.544		.544	88.5				
119.7	+.23	.436	.352	.065	.318		.318	93.3			3.89	59.8
179.9	+.19	.441	.357	.066	.238		.238	95.0			2.99	45.3
302.6	+.19	.446	.362	.066	.183		.183	96.1			(1.95)	
Average	+.32	.415	.357	.071						418		52.6
					d-TALOSE							
0					(4.903)	2.164	2.739	0.0				
0.9	+0.27	0.362	0.386	0.094	4.530	1.836	2.694	7.6				
4.8	+.45	.373	.383	.090	3.470	.953	2.517	29.2	73.0	811		
10.0	+.46	.384	.379	.086	2.720	.405	2.315	44.5	72.1	838		
20.0	+.38	.396	.381	.083	2.052	.072	1.980	58.1	73.6	887		
30.7	+.31	.404	.381	.081	1.685		1.685	65.6				
45.2	+.26	.411	.377	.077	1.330		1.330	72.9			7.09	92.1
75.3	+.22	.421	.378	.076	.871		.871	82.2			6.43	84.6
121.8	+.21	.430	.387	.077	.480		.480	90.2			5.99	77.8
Average	+.32	.398	.382	.083						844		84.8
					l-ARABINOSE							
0	(+0.12)				(3.930)	2.655	1.275	0.0				
1.0	+.62	0.364	0.360	0.084	3.200	1.946	1.254	18.6				
2.9	+.80	.376	.358	.080	2.367	1.148	1.219	39.8	120.5	1,506		
6.9	+.84	.393	.355	.073	1.526	.370	1.156	61.2	122.2	1,674		
15.0	+.34	.409	.354	.071	1.082	.045	1.037	72.5	116.8	1,645		
30.0	+.19	.421	.351	.068	.858		.858	78.2				
60.0	+.20	.430	.351	.066	.578		.578	85.3			5.72	86.7
107.2	+.14	.437	.350	.065	.327		.327	91.7			5.43	83.5
150.0	+.14	.441	.350	.064	.200		.200	94.9			5.27	82.3
209.7	+.14	.444	.351	.064	.125		.125	96.8			(4.66)	(72.8)
269.9	+.11	.447	.351	.063	.087		.087	97.8			(4.14)	(65.7)
Average	+.35	.416	.353	.070						1,608		84.2

TABLE 8.—*Bromine oxidations of aqueous sugar solutions in equilibrium at the beginning of the oxidation*—Continued

Time	Temperature	Averages for the oxidation period			Unoxidized sugar			Oxidized sugar	Velocity constants			
		Bromide (Br^-)	Bromine (Br_2)	Free bromine (a)	Total	More reactive fraction	Less reactive fraction		More reactive fraction		Less reactive faction	
									$ak_B \times 10^3$	$k_B \times 10^3$	$ak_A \times 10^3$	$k_A \times 10^3$
1	2	3	4	5	6	7	8	9	10	11	12	13
					d-XYLOSE							
0	(+0.19)				(3.938)	2.675	1.263	0.0				
0.9	+.41	0.365	0.351	0.081	3.267	2.020	1.247	17.0				
4.7	+.64	.385	.348	.075	1.809	.625	1.184	54.1	134.1	1,788		
9.8	+.57	.402	.346	.070	1.301	.188	1.113	67.0	115.9	1,656		
14.9	+.50	.410	.345	.068	1.112	.064	1.048	71.8	107.1	1,575		
29.9	+.35	.421	.343	.065	.882		.882	77.6				
60.1	+.28	.430	.342	.063	.607		.607	84.6			5.37	85.2
120.1	+.23	.438	.343	.062	.310		.310	92.1			5.03	81.1
180.0	+.21	.443	.343	.061	.183		.183	95.4			4.55	74.6
240.0	+.20	.445	.344	.061	.124		.124	96.9			(4.06)	(66.6)
353.4	+.20	.449	.346	.061	.074		.074	98.1			(3.33)	(54.6)
Average	+.36	.419	.345	.067						1,673		80.3
					d-LYXOSE							
0					(3.740)	0.758	2.982	0.0				
0.9	+0.27	0.361	0.386	0.095	3.530	.658	2.872	5.6				
5.0	+.41	.372	.383	.090	2.800	.348	2.452	25.1	67.5	750		
9.9	+.42	.381	.379	.086	2.250	.194	2.056	39.8	58.9	685		
20.1	+.39	.395	.363	.077	1.517		1.517	59.4				
29.9	+.36	.404	.369	.077	1.111		1.111	70.3			13.8	179
44.9	+.32	.414	.365	.073	.686		.686	81.7			13.9	190
59.8	+.28	.421	.362	.071	.423		.423	88.7			14.0	197
90.7	+.24	.432	.359	.068	.111		.111	97.0			(16.1)	(237)
Average	+.34	.398	.372	.080						717		189
					d-RIBOSE							
0	(+0.07)				(3.716)	0.396	3.320	0.0				
0.7	+.35	0.358	0.378	0.093	3.572	.340	3.232	3.9				
2.7	+.38	.362	.377	.091	3.220	.222	2.998	13.3	92.6	1,018		
6.6	+.40	.370	.373	.087	2.720	.104	2.616	26.8	87.2	1,002		
14.7	+.28	.382	.366	.082	2.012		2.012	45.9				
29.8	+.23	.398	.360	.075	1.210		1.210	67.4			14.6	195
61.4	+.14	.416	.357	.070	.522		.522	86.0			12.5	179
119.9	+.14	.432	.363	.069	.127		.127	96.6			11.4	165
179.9	+.14	.440	.363	.068	.039		.039	99.0			(10.4)	(153)
Average	+.26	.395	.367	.079						1,010		180
					l-RIBOSE							
0	(+0.20)				(4.096)	0.452	3.644	0.0				
0.9	+.35	0.358	0.387	0.096	3.861	.338	3.523	5.7				
2.4	+.45	.361	.386	.095	3.515	.186	3.329	14.2	172.9	1,820		
7.1	+.47	.370	.382	.090	2.920	.083	2.837	28.7	98.4	1,093		
14.9	+.48	.382	.379	.086	2.208		2.208	46.1				
29.9	+.48	.397	.374	.080	1.371		1.371	66.5			13.8	173
45.0	+.40	.408	.372	.077	.902		.902	78.0			12.9	168
60.1	+.35	.416	.371	.075	.586		.586	85.7			12.7	169
180.0	+.30	.440	.369	.069	.050		.050	98.8			(10.0)	(145)
Average	+.41	.392	.378	.083						1,456		170

TABLE 8.—*Bromine oxidations of aqueous sugar solutions in equilibrium at the beginning of the oxidation*—Continued

Time	Temperature	Averages for the oxidation period			Unoxidized sugar			Oxidized sugar	Velocity constants			
		Bromide (Br^-)	Bromine (Br_2)	Free bromine (a)	Total	More reactive fraction	Less reactive fraction		More reactive fraction		Less reactive fraction	
									$ak_B \times 10^3$	$k_B \times 10^3$	$ak_A \times 10^3$	$k_A \times 10^3$
1	2	3	4	5	6	7	8	9	10	11	12	13
					l-RHAMNOSE							
0	(+0.17)				(4.260)	1.321	2.939	0.0				
1.0	+.33	0.359	0.374	0.091	4.012	1.124	2.888	5.8				
3.9	+.36	.365	.370	.088	3.478	.727	2.751	18.4	65.3	742		
8.0	+.49	.372	.367	.084	2.970	.387	2.583	30.3	66.2	788		
15.1	+.46	.381	.364	.081	2.468	.145	2.323	42.1	63.1	779		
30.0	+.39	.393	.361	.077	1.886		1.886	55.7				
61.4	+.31	.408	.356	.072	1.211		1.211	71.6			6.13	85.1
120.0	+.25	.421	.350	.067	.573		.573	86.6			5.75	85.8
185.1	+.23	.430	.349	.066	.290		.290	93.2			5.24	79.4
240.2	+.22	.435	.349	.065	.184		.184	95.7			(4.81)	(74.0)
300.2	+.21	.439	.349	.064	.135		.135	96.8			(4.24)	(66.3)
Average	+.33	.400	.359	.075						770		83.4
					LACTOSE							
0					(9.399)	5.876	3.523	0.0				
0.7	+0.29	0.361	0.369	0.089	8.150	4.639	3.511	13.3				
3.0	+.65	.377	.364	.082	5.160	1.699	3.461	45.1	114.8	1,435		
10.0	+.70	.402	.358	.074	3.470	.128	3.342	63.1	110.6	1,515		
29.5	+.43	.419	.353	.069	3.190		3.190	66.1				
60.3	+.30	.425	.353	.067	2.870		2.870	69.5			1.53	22.5
120.1	+.22	.430	.352	.066	2.358		2.358	74.9			1.46	21.8
183.7	+.20	.435	.351	.065	1.959		1.959	79.2			1.41	21.0
240.2	+.19	.439	.351	.064	1.661		1.661	82.3			1.35	20.1
364.3	+.18	.443	.351	.064	1.421		1.421	84.9			1.29	19.0
Average	+.35	.415	.356	.071						1,475		20.9
					MALTOSE							
0	(+0.21)				(9.421)	5.871	3.550	0.0				
0.8	+.42	0.362	0.375	0.090	8.200	4.664	3.536	13.0				
3.8	+.66	.377	.373	.085	5.640	2.152	3.488	40.1	112.0	1,318		
7.9	+.70	.390	.371	.081	4.160	.732	3.428	55.8	113.3	1,399		
14.9	+.60	.402	.367	.077	3.460	.125	3.335	63.3	111.5	1,448		
30.0	+.43	.412	.362	.073	3.150		3.150	66.6				
60.0	+.32	.419	.360	.071	2.760		2.760	70.7			1.91	26.9
100.1	+.27	.423	.359	.070	2.371		2.371	74.8			1.76	25.1
162.1	+.24	.428	.360	.069	1.908		1.908	79.7			1.65	23.9
207.0	+.23	.430	.360	.069	1.675		1.675	82.2			1.55	22.5
360.0	+.20	.435	.365	.069	1.092		1.092	88.4			1.39	20.1
Average	+.41	.408	.365	.075						1,388		23.7

A comparison of the results obtained with the freshly dissolved crystalline sugars (table 7) with those for the equilibrium solutions (table 8) shows that in each case a part of the sugar is oxidized rapidly while the rest is oxidized slowly. In order to calculate the velocity constants and the proportions of the more reactive and of the less reactive sugar the oxidation is divided into two periods, a short period beginning at zero time, during which a rapid oxidation occurs, and a long period beginning when the rapid change is substantially complete. The time selected for the beginning of the calculations for each of the sugars is that given in the table for the sample immediately preceding the first recorded value of ak_A. By applying equation 7 to the data representing the long period (that is, the data representing the latter part of the oxidation) values of ak_A are obtained. The values of k_A are then obtained by dividing by a, the concentration of the free bromine given in column 5. Using the average value of k_A, values of ak_A are calculated for each of the samples taken during the initial period, using the corresponding value of a. The slow oxidation is then extrapolated to times corresponding to the taking of the earlier samples by means of equation 7, thereby obtaining values for the less reactive unoxidized sugar. The difference between the total sugar (obtained by analysis) and the less reactive sugar gives the amount of the more reactive sugar, which amount is reported in column 7. Application of equation 7 to these data gives the values of ak_B reported in column 10. The values of k_B are arrived at by dividing by a. Since the slowly oxidizable substance appears to be largely the normal alpha isomer, and the rapidly oxidizable material the beta form, the constants k_A and k_B are analogous to the constants k_α and k_β obtained by the oxidation of the crystalline sugars. To ascertain the quantity of more reactive sugar in the original solution the rapid reaction is extrapolated to zero time by means of equation 7 in a manner analogous to that used for obtaining the quantities of less reactive sugar. These calculations provide the velocity constants and the proportions of the less reactive and more reactive sugars in the equilibrium solutions.

In order to determine if there were any detectable difference in the behavior of solutions of galactose in equilibrium at different temperatures, solutions of this sugar were prepared at 20° C and at 0° C and oxidized. The oxidation of the sugar solution in equilibrium at 0° C was conducted as usual; the oxidation of the sugar solution in equilibrium at 20° C was conducted in like manner except that compensation was made for the difference in temperature by cooling the oxidant (before adding the sugar solution) below 0° C. The amount of cooling was adjusted so that on mixing the sugar solution at 20° C with the cold oxidant the temperature of the solution rose to approximately 0° C. No difference in the results obtained in the two experiments could be detected.

The oxidation of freshly dissolved (*d*-gulose)$_2$ $CaCl_2.H_2O$ shows the presence of two modifications of the sugar and consequently it was handled like an equilibrium solution. The results, which were discussed on page 161, are given in table 9.

TABLE 9.—*Bromine oxidation of freshly dissolved (d-gulose)$_2$ $CaCl_2.H_2O$*

Time	Temperature	Averages for the oxidation period			Unoxidized sugar			Oxidized sugar	Velocity constants			
									More reactive fraction		Less reactive fraction	
		Bromide (Br^-)	Bromine (Br_2)	Free bromine (a)	Total	More reactive fraction	Less reactive fraction		$ak_B \times 10^3$	$k_B \times 10^3$	$ak_A \times 10^3$	$k_A \times 10^3$
1	2	3	4	5	6	7	8	9	10	11	12	13
Minutes	°C	*Moles/liter*	*Moles/liter*	*Moles/liter*	g	g	g	*Percent*				
0	+0.17	0.358			(4.635)	1.485	3.150	0				
0.8	+.29	.368	0.375	0.088	4.530	1.408	3.122	2.3				
4.9	+.43	.401	.370	.088	4.060	1.077	2.983	12.4	28.4	323		
30.0	+.28	.418	.362	.080	2.562	.235	2.327	44.7	26.6	333		
60.0	+.21	.436	.357	.075	1.785		1.785	61.5				
124.7	+.22	.443	.350	.069	.990		.990	78.6			3.96	57.4
179.9	+.17	.450	.348	.067	.682		.682	85.3			3.49	52.1
300.2	+.14		.350	.066	.381		.381	91.8			(2.79)	(42.3)
Average										328		54.8

3. MUTAROTATION MEASUREMENTS

The optical rotations, with the exception of the thermal mutarotations, were measured in a 4-dm Schmidt and Haensch water-jacketed glass tube on a Bates saccharimeter. For reducing saccharimeter readings to angular degrees, Bates and Jackson [98, 99] obtained the conversion factor 0.34620 for sucrose. The carefully purified sugars were dried at 50° C, powdered in an agate mortar, and passed through a fine sieve. The weighed sample (usually 2 g) was placed in a dry 100-ml glass-stoppered flask and about 50 ml of pure distilled water at the correct temperature (either 20 or 0° C) was added quickly with agitation, from a pipette which had the tip cut off so that it drained in about 10 seconds. Time was measured with a stop watch, starting with the addition of the water. About 10 seconds were required to dissolve the sugar. The measurements at 20° C were conducted in a room held at about 19.5° C, while those at 0° C were conducted in essentially the same manner except that the flasks and the solutions were cooled in ice water. The readings were made by one observer while another measured the time and recorded the results. The separate readings given in tables 10 and 11 represent the average of five or more consecutive observations. The method used for the calculations of the velocity constants and the initial rotations is given on page 156.

TABLE 10.—*First-order mutarotations*

α-d-GLUCOSE					
3.9 g per 100 ml at 0.2° C read in a 4-dm tube $°S = 23.74 + 27.05 \times 10^{-0.007411t}$ $[\alpha]_D^{0.2} = 2.1946 \times °S$			3.9 g per 100 ml at 20° C read in a 4-dm tube $°S = 23.94 + 27.01 \times 10^{-0.003331t}$ $[\alpha]_D^{20} = 2.2013 \times °S$		
Time	Observed reading	$(k_1+k_2)\times 10^3$	Time	Observed reading	$(k_1+k_2)\times 10^3$
Minutes	°S		*Minutes*	°S	
2.70	+50.67		1.59	+50.33	
3.89	+50.60	(0.950)	2.56	+49.98	(5.98)
6.84	+50.46	(.821)	4.76	+49.15	6.27
10.58	+50.31	.742	7.44	+48.13	6.46
15.44	+50.08	.755	9.93	+47.29	6.37
24.91	+49.61	.785	16.36	+45.19	6.37
41.48	+48.90	.761	20.63	+43.92	6.35
60.08	+48.14	.747	25.51	+42.53	6.36
90.80	+46.93	.737	30.03	+41.39	6.32
120.34	+45.84	.730	39.94	+39.07	6.30
182.52	+43.63	.732	49.83	+37.01	6.33
240.68	+41.81	.728	59.95	+35.27	6.29
299.05	+40.10	.730	75.01	+33.08	6.27
409.4	+37.34	.730	89.84	+31.28	6.30
556.0	+34.34	.732	120.94	+28.62	6.29
747.4	+31.44	.730	169.19	+26.31	6.25
1,352.1	+26.50	.733	∞	+23.94	
∞	+23.74				
Average..		.741	Average..		6.32

β-d-GLUCOSE					
3.9 g per 100 ml at 0.2° C read in a 4-dm tube $°S = 23.66 - 15.29 \times 10^{-0.007384t}$ $[\alpha]_D^{0.2} = 2.2020 \times °S$			3.9 g per 100 ml at 20° C read in a 4-dm tube $°S = 23.98 - 15.45 \times 10^{-0.003381t}$ $[\alpha]_D^{20} = 2.1927 \times °S$		
3.02	+8.45		1.48	+8.86	
4.59	+8.48	(.548)	2.46	+9.06	(5.90)
10.01	+8.68	(.947	4.96	+9.57	6.00
21.83	+8.92	.725	9.91	+10.57	6.18
39.84	+9.39	.753	14.96	+11.52	6.23
59.90	+9.85	.737	19.96	+12.39	6.25
90.00	+10.56	.746	29.95	+13.96	6.28
120.17	+11.19	.736	45.32	+15.95	6.27
181.9	+12.45	.741	60.04	+17.53	6.32
246.8	+13.61	.738	90.07	+19.81	6.31
302.6	+14.56	.745	120.20	+21.80	6.33
390.4	+15.80	.740	183.95	+22.93	6.35
544.6	+17.60	.738	∞	+23.98	
1,366.3	+22.09	.723			
∞	+23.66				
Average..		.738	Average..		6.25

TABLE 10.—*First-order mutarotations*—Continued

Time	Observed reading	$(k_1+k_2)\times10^3$	Time	Observed reading	$(k_1+k_2)\times10^3$
α-d-MANNOSE					
4.0 g per 100 ml at 0.1° C read in a 4-dm tube $°S=6.63+6.47\times10^{-.00215t}$ $[\alpha]^{0.1}_D=2.2021\times°S$			4.0 g per 100 ml at 20° C read in a 4-dm tube $°S=6.63+7.07\times10^{-.0172t}$ $[\alpha]^{20}_D=2.1418\times°S$		
Minutes	° S		*Minutes*	° S	
3.80	+12.98		1.74	+13.23	
7.63	+12.84	(2.53)	3.10	+12.86	(18.4)
10.10	+12.78	2.20	4.60	+12.51	17.5
14.98	+12.66	2.01	7.25	+11.93	17.3
29.98	+12.24	2.06	9.96	+11.39	17.3
45.13	+11.77	2.22	15.66	+10.43	17.2
59.95	+11.44	2.15	20.80	+9.71	17.4
89.99	+10.76	2.17	30.25	+8.75	17.3
121.17	+10.16	2.17	39.90	+8.06	17.4
240.67	+8.53	2.21	50.18	+7.59	17.3
300.33	+8.02	2.22	62.29	+7.24	17.1
421.96	+7.40	2.19	90.10	+6.87	(16.3)
∞	+6.63		∞	+6.63	
Average		2.16	Average		17.3
β-d-MANNOSE					
4.0 g per 100 ml at 0.3° C read in a 4-dm tube $°S=6.66-14.28\times10^{-.00214t}$ $[\alpha]^{0.3}_D=2.1922\times°S$			4.0 g per 100 ml at 20.1° C read in a 4-dm tube $°S=6.38-14.01\times10^{-.0178t}$ $[\alpha]^{20.1}_D=2.2257\times°S$		
2.64	−7.44		2.20	−6.42	
5.53	−7.27	(1.82)	3.59	−5.72	17.6
20.19	−6.28	2.12	6.64	−4.29	17.9
44.88	−4.79	2.14	10.13	−2.85	17.9
59.93	−3.99	2.13	15.48	−1.12	17.5
90.03	−2.46	2.17	20.05	+.16	17.6
120.31	−1.21	2.15	29.90	+2.21	17.6
180.00	+.79	2.15	39.94	+3.62	17.7
240.10	+2.29	2.14	49.99	+4.56	17.7
299.90	+3.39	2.14	60.01	+5.20	17.9
363.30	+4.27	2.14	78.45	+5.87	18.4
420.30	+4.81	2.11	99.76	+6.21	(19.2)
∞	+6.66		∞	+6.38	
Average		2.14	Average		17.8
α-d-GULOSE $CaCl_2.H_2O$					
6.468 g per 100 ml at 0.2° C read in a 4-dm tube $°S=-6.79+36.08\times10^{-.00198t}$ $[\alpha]^{0.2}_D=1.3844\times°S$			6.807 g per 100 ml at 20° C read in a 4-dm tube $°S=-7.85+37.00\times10^{-.0191t}$ $[\alpha]^{20}_D=1.2739\times°S$		
2.85	+28.85		3.17	+24.33	
6.44	+28.30	1.88	4.63	+22.28	19.6
14.88	+27.08	1.84	7.46	+18.71	19.4
29.84	+24.85	1.92	10.38	+15.57	19.1
60.06	+20.88	1.92	16.30	+10.23	19.1
119.94	+14.59	1.90	21.04	+6.85	19.0
183.42	+9.48	1.89	25.86	+4.10	19.0
239.9	+5.97	1.88	29.93	+2.16	19.0
299.7	+3.11	1.87	39.63	−1.30	19.0
397.5	−.25	1.87	49.92	−3.67	19.0
567.5	−3.62	1.86	60.09	−5.16	18.9
739.5	−5.33	1.88	76.31	−6.56	19.1
∞	−6.79		∞	−7.85	
Average		1.88	Average		19.1

TABLE 10.—*First-order mutarotations*—Continued

Time	Observed reading	$(k_1+k_2)\times10^2$	Time	Observed reading	$(k_1+k_2)\times10^2$
(*d*-GULOSE)$_2$ $CaCl_2.H_2O$					
4.215 g per 100 ml at 0.2° C read in a 4-dm tube $°S=-8.01+24.40\times10^{-.00202t}$ $[\alpha]^{0.2}D=2.1099\times°S$			4.281 g per 100 ml at 20.1° C read in a 4-dm tube $°S=-7.88+21.94\times10^{-.0197t}$ $[\alpha]^{20.1}D=2.0939\times°S$		
Minutes	°S		*Minutes*	°S	
2.68	+16.09		2.13	+13.85	
5.86	+15.74	2.00	3.46	+12.64	18.7
14.90	+14.73	2.06	5.77	+10.50	20.0
29.88	+13.16	2.07	11.31	+6.41	19.8
44.99	+11.76	2.03	15.26	+4.02	19.9
60.00	+10.46	2.02	19.84	+1.82	19.8
91.36	+7.91	2.03	25.76	−.07	18.8
139.76	+4.72	2.02	30.07	−1.77	19.7
181.61	+2.52	2.01	40.62	−4.11	19.8
244.20	−.15	2.01	49.92	−5.41	19.8
300.78	−1.94	2.01	61.30	−6.45	20.0
361.76	−3.42	2.01	75.30	−7.15	20.1
∞	−8.01		∞	−7.88	
Average		2.02	Average		19.7
***α*-*d*-XYLOSE**					
4.2 g per 100 ml at 0° C read in a 4-dm tube $°S=8.46+38.09\times10^{-.00248t}$ $[\alpha]^{0.0}D=2.0449\times°S$			4.4 g per 100 ml at 20° C read in a 4-dm tube $°S=9.58+38.10\times10^{-.0207t}$ $[\alpha]^{20}D=1.9624\times°S$		
3.0	+45.91		1.6	+44.93	
5.9	+45.30	2.46	2.5	+43.53	(19.5)
15.0	+43.49	2.42	4.2	+40.96	19.9
20.0	+42.45	2.48	6.5	+37.71	20.2
29.9	+40.60	2.47	10.6	+32.77	20.3
49.8	+37.20	2.46	15.0	+28.39	20.4
76.1	+33.25	2.45	25.0	+21.34	20.4
104.7	+29.50	2.46	34.9	+16.99	20.4
156.6	+24.21	2.45	40.1	+15.43	20.3
210.1	+20.08	2.45	49.8	+13.27	20.4
270.2	+16.77	2.45	60.0	+11.89	20.3
374.4	+13.94	2.44	98.0	+10.00	(20.0)
∞	+8.46		∞	+9.58	
Average		2.45	Average		20.3
***α*-*d*-LYXOSE**					
3.9 g per 100 ml at 0.2° C read in a 4-dm tube $°S=-6.09+8.20\times10^{-.00844t}$ $[\alpha]^{0.1}D=2.2003\times°S$			4.0 g per 100 ml at 20° C read in a 4-dm tube $°S=-6.46+9.10\times10^{-.0363t}$ $[\alpha]^{20}D=2.1362\times°S$		
2.92	+1.66		1.71	+0.82	
5.77	+1.24	8.49	1.92	+.63	54.7
9.99	+.66	8.49	2.25	+.36	52.5
15.01	+.10	8.07	3.45	−.59	53.7
20.20	−.49	8.17	4.74	−1.52	55.6
26.11	−1.11	8.28	5.86	−2.27	57.8
30.12	−1.54	8.50	7.80	−3.26	58.6
40.05	−2.32	8.43	16.10	−4.13	59.0
50.11	−3.00	8.46	12.99	−4.91	59.6
59.90	−3.63	8.75	17.64	−5.64	59.5
89.79	−4.67	8.48	27.10	−6.21	57.7
120.01	−5.35	8.71	30.26	−6.28	56.3
∞	−6.09		∞	−6.46	
Average		8.44	Average		56.8

TABLE 10.—*First-order mutarotations*—Continued

β-d-LYXOSE					
4.0 g per 100 ml at 0° C read in a 4-dm tube $°S = -6.12 - 26.20 \times 10^{-.0034t}$ $[\alpha]^{t}_{D} = 2.1895 \times °S$			4.0 g per 100 ml at 20° C read in a 4-dm tube $°S = -6.43 - 27.39 \times 10^{-.0031t}$ $[\alpha]^{20}_{D} = 2.1462 \times °S$		
Time	Observed reading	$(k_1+k_2)\times 10^3$	Time	Observed reading	$(k_1+k_2)\times 10^3$
Minutes	°S		*Minutes*	°S	
2.02	−31.31		1.56	−28.58	
4.91	−29.89	8.71	2.33	−26.40	58.4
10.01	−27.64	8.56	3.18	−24.26	58.2
15.02	−25.71	8.40	3.69	−23.04	58.7
19.96	−23.94	8.38	4.40	−21.55	58.4
24.84	−22.34	8.38	5.57	−19.30	58.8
29.97	−20.85	8.34	6.65	−17.50	59.2
40.72	−18.08	8.36	7.58	−16.17	59.3
50.88	−15.99	8.33	9.73	−13.67	59.4
60.10	−14.43	8.29	12.14	−11.64	59.4
90.59	−10.73	8.33	20.04	−8.14	60.2
119.70	−8.74	8.35	29.90	−6.87	60.1
∞	−6.12		∞	−6.43	
Average..		8.40	Average..		59.1

α-*l*-RHAMNOSE. H_2O					
4.5 g per 100 ml at 0° C read in a 4-dm tube $°S = 4.56 - 8.46 \times 10^{-.0036t}$ $[\alpha]^{t}_{D} = 1.9079 \times °S$			4.0 g per 100 ml at 20.2° C read in a 4-dm tube $°S = 3.81 - 7.81 \times 10^{-.0430t}$ $[\alpha]^{20.2}_{D} = 2.1522 \times °S$		
3.1	−3.56		1.43	−2.97	
10.1	−2.83	5.85	1.84	−2.71	41.4
15.2	−2.37	5.69	2.37	−2.39	41.3
30.3	−1.05	5.90	3.65	−1.66	42.0
42.1	−.35	5.60	5.08	−.95	42.1
60.2	+.65	5.56	7.68	+.21	44.0
75.4	+1.40	5.67	9.93	+.91	43.4
91.5	+1.98	5.63	15.31	+2.16	44.2
119.7	+2.77	5.63	20.24	+2.82	44.4
149.9	+3.36	5.66	24.92	+3.15	43.1
180.2	+3.77	5.71	29.96	+3.43	43.9
241.2	+4.19	5.63	40.89	+3.72	
∞	+4.56		∞	+3.81	
Average..		5.68	Average..		43.0

α-LACTOSE . H_2O					
4.9 g per 100 ml at 0.2° C read in a 4-dm tube $°S = 30.43 + 18.60 \times 10^{-.0035t}$ $[\alpha]^{0.2}_{D} = 1.7614 \times °S$			7.2 g per 100 ml at 20° C read in a 4-dm tube $°S = 46.15 + 28.40 \times 10^{-.0037t}$ $[\alpha]^{20}_{D} = 1.1398 \times °S$		
5.19	+48.91		1.98	+73.95	
10.06	+48.80	0.532	2.95	+73.61	4.67
20.76	+48.54	.564	4.83	+73.09	4.79
59.90	+47.69	.542	10.42	+71.52	4.71
120.26	+46.48	.532	20.05	+69.04	4.67
181.2	+45.28	.540	30.04	+66.67	4.70
241.5	+44.18	.543	60.12	+60.98	4.69
401.5	+41.66	.546	91.00	+56.76	4.70
590.9	+39.30	.544	119.93	+53.91	4.70
832.4	+37.00	.543	180.50	+50.17	4.70
1,347.3	+33.84	.547	239.80	+48.19	4.77
1,834.4	+32.28	.546	∞	+46.15	
∞	+30.43				
Average..		0.544	Average..		4.71

TABLE 10.—*First-order mutarotations*—Continued

β-LACTOSE					
3.9 g per 100 ml at 0.2° C read in a 4-dm tube $°S = 25.56 - 9.09 \times 10^{-.0005341}$ $[\alpha]^{0.2}_D = 2.2066 \times °S$			4.0 g per 100 ml at 20° C read in a 4-dm tube $°S = 25.34 - 9.38 \times 10^{-.004681}$ $[\alpha]^{20}_D = 2.1863 \times °S$		
Time	Observed reading	$(k_1+k_2)\times 10^3$	Time	Observed reading	$(k_1+k_2)\times 10^3$
Minutes	°S		*Minutes*	°S	
4.85	+16.52	----------	1.97	+16.16	----------
10.22	+16.59	(0.629)	3.16	+16.27	(4.39)
30.28	+16.80	.538	5.04	+16.42	(4.07)
59.96	+17.08	.504	10.06	+16.91	4.57
120.51	+17.71	.530	19.91	+17.76	4.64
240.4	+18.78	.531	30.10	+18.54	4.63
384.8	+19.82	.519	60.03	+20.46	4.73
549.3	+20.89	.527	89.71	+21.78	4.69
801.8	+22.13	.528	120.24	+22.77	4.67
1,340.6	+23.79	.530	149.50	+23.48	4.70
1,892.7	+24.57	.509	182.80	+24.02	4.66
2,842.8	+25.26	.521	244.10	+24.66	4.67
∞	+25.56	----------	∞	+25.34	----------
Average	----------	0.524	Average	----------	4.66
β-MALTOSE. H_2O					
4.5 g per 100 ml at 0° C read in a 4-dm tube $°S = 68.80 - 8.75 \times 10^{-.0003301}$ $[\alpha]^0_D = 1.9113 \times °S$			4.2 g per 100 ml at 20° C read in a 4-dm tube $°S = 62.81 - 9.00 \times 10^{-.003271}$ $[\alpha]^0_D = 2.0761 \times °S$		
4.9	+60.11	----------	2.33	+54.06	----------
22.8	+60.34	0.583	3.46	+54.18	5.31
31.1	+60.45	.593	5.38	+54.39	5.48
62.2	+60.83	.585	10.13	+54.85	5.27
120.2	+61.46	.565	19.92	+55.74	5.26
182.1	+62.09	.560	29.93	+56.53	5.22
241.8	+62.72	.576	59.95	+58.44	5.23
300.1	+63.28	.583	103.96	+60.22	5.20
353.3	+63.70	.577	137.43	+61.09	5.23
487.2	+64.71	.580	180.11	+61.78	5.23
686.8	+65.93	.584	240.00	+62.32	5.27
1406.	+68.35	.589	300.90	+62.61	(5.50)
∞	+68.80	----------	∞	+62.81	----------
Average	----------	0.580	Average	----------	5.27

TABLE 11.—*Complex mutarotations of sugars in water*

α-*l*-ARABINOSE

4.1 g per 100 ml at 0° C read in a 4-dm tube $°S = 37.74\times10^{-.0886t} + 2.83\times10^{-.0217t} + 52.20$ $[\alpha]^5_D = °S\times2.0920$						5.0 g per 100 ml at 20° C read in a 2-dm tube $°S = 22.13\times10^{-.0304t} + 2.53\times10^{-.1314t} + 29.92$ $[\alpha]^{20}_D = °S\times3.4926$					
Time	Observed reading	$(k_1+k_2)\times10^3$	$m_1\times10^3$	Deviation	$m_2\times10^3$	Time	Observed reading	$(k_1+k_2)\times10^3$	$m_1\times10^3$	Deviation	$m_2\times10^3$
1	2	3	4	5	6	1	2	3	4	5	6
Minutes	° S			° S		*Minutes*	° S			° S	
4.3	+90.89			+2.28		2.1	+50.36			+1.30	
6.6	+89.94	4.70		+2.02	22.9	3.1	+48.70	36.8		+.91	155
9.9	+88.70	4.52		+1.75	20.5	5.1	+46.00	34.7		+.52	133
15.3	+86.75	4.47		+1.33	21.3	7.1	+43.70	34.2		+.23	150
19.9	+85.16	4.46		+.99	23.2	10.1	+41.10	32.8		+.16	114
25.0	+83.66	4.34		+.82	21.5	15.0	+37.78	32.2		(+.01)	
29.8	+82.29	4.28		+.65	21.4	20.0	+35.48	31.6			
40.3	+79.59	4.17		+.42	20.4	30.0	+32.70	31.1	30.1		
60.4	+75.01	4.09				40.0	+31.36	30.4	29.3		
90.0	+69.94	3.95	3.69			60.0	+30.29	30.1	29.4		
109.8	+67.26	3.88	3.65			75.0	+30.03	31.1	31.0		
135.5	+64.33	3.84	3.65			90.00	+29.94				
166.2	+61.57	3.80	3.65			∞	+29.92				
197.0	+59.49	3.76	3.63								
240.3	+57.33	3.72	3.60								
300.0	+55.38	3.67	3.57								
448.4	+53.16	3.61	3.55								
∞	+52.20										
Average			3.62		21.7	Average			30.0		138

β-*l*-ARABINOSE $CaCl_2.4H_2O$

β-L-ARABINOSE $CaCl_2.4H_2O$

9.3 g per 100 ml at 0° C read in a 4-dm tube $^{\circ}S = -18.01\times10^{-.003t} + 2.23\times10^{-.030t} + 53.63$ $[\alpha]_D^t = {}^{\circ}S\times0.9342$						8.9 g per 100 ml at 20.0° C read in a 4-dm tube $^{\circ}S = -17.29\times10^{-.030t} + 3.58\times10^{-.169t} + 49.33$ $[\alpha]_D^{20} = {}^{\circ}S\times0.9730$					
3.0	+37.82	----------	----------	+1.73	----------	1.40	+36.13	----------	----------	+2.50	----------
6.0	+37.85	----------	----------	+1.30	41.4	2.32	+36.32	6.8	----------	+1.72	177
10.3	+38.11	1.10	----------	+.92	37.6	2.90	+36.58	10.0	----------	+1.40	168
12.7	+38.30	1.38	----------	+.76	36.8	3.58	+36.92	12.3	----------	+1.09	165
15.0	+38.51	1.61	----------	+.65	35.4	4.86	+37.61	14.9	----------	+.64	171
19.9	+38.98	1.96	----------	+.45	34.6	6.09	+38.40	17.5	----------	+.42	165
24.8	+39.41	2.11	----------	+.24	39.4	10.46	+40.96	21.8	----------	+.02	----------
29.8	+40.01	2.42	----------	+.22	33.4	19.91	+44.96	25.9	----------	----------	----------
42.6	+41.42	2.83	----------	+.15	(26.8)	25.03	+46.28	26.9	30.5	----------	----------
62.3	+43.25	3.08	----------	----------	----------	29.94	+47.15	27.4	30.1	----------	----------
90.1	+45.54	3.34	3.89	----------	----------	40.17	+48.23	27.8	29.6	----------	----------
120.8	+47.41	3.44	3.80	----------	----------	50.13	+48.79	28.5	30.0	----------	----------
180.5	+50.00	3.60	3.87	----------	----------	60.28	+49.02	27.7	(28.5)	----------	----------
212.1	+50.81	3.58	3.78	----------	----------	∞	+49.33	----------	----------	----------	----------
250.0	+51.68	3.68	3.87	----------	----------	----------	----------	----------	----------	----------	----------
307.6	+52.46	3.71	3.86	----------	----------	----------	----------	----------	----------	----------	----------
351.2	+52.80	3.68	3.80	----------	----------	----------	----------	----------	----------	----------	----------
∞	+53.63	----------	----------	----------	----------	----------	----------	----------	----------	----------	----------
Average	----------	----------	3.84	----------	36.9	Average	----------	----------	30.0	----------	169

TABLE 11.—*Complex mutarotations of sugars in water*—Continued

α-d-GALACTOSE

4.1 g per 100 ml at 0° C read in a 4-dm tube $°S=31.70\times10^{-.000334t}+1.31\times10^{-.01194t}+40.19$ $[\alpha]_D^0=°S\times2.0901$						5.0 g per 100 ml at 20.0° C read in a 4-dm tube $°S=37.51\times10^{-.000331t}+3.25\times10^{-.0791t}+46.34$ $[\alpha]_D^{20}=°S\times1.7307$					
Time	Observed reading	$(k_1+k_2)\times10^3$	$m_1\times10^3$	Deviation	$m_2\times10^3$	Time	Observed reading	$(k_1+k_2)\times10^3$	$m_1\times10^3$	Deviation	$m_2\times10^3$
1	2	3	4	5	6	1	2	3	4	5	6
Minutes	° S			° S		*Minutes*	° S			° S	
3.3	+72.87			+1.20		1.9	+84.85			+2.30	
10.1	+72.24	1.24		+1.03	9.6	3.0	+83.67	12.3		+1.84	88.1
15.2	+71.75	1.27		+.86	12.1	4.4	+82.44	11.3		+1.52	72.0
19.7	+71.40	1.22		+.81	10.4	6.6	+80.54	11.0		+1.00	77.0
29.9	+70.51	1.22		+.58	11.9	8.6	+79.03	10.6		+.69	78.0
39.9	+69.72	1.20		+.43	12.2	10.2	+77.95	10.3		+.55	74.9
49.8	+68.93	1.20		+.25	14.6	12.0	+76.73	10.2		+.34	83.9
59.6	+68.34	1.15		+.24	12.4	14.8	+75.09	9.8		+.22	79.0
90.7	+66.36	1.10				29.7	+68.00	9.0			
120.4	+64.69	1.07				45.0	+62.66	8.7	8.04		
181.2	+61.65	1.03	0.947			59.8	+58.75	8.5	8.04		
240.2	+59.11	1.00	.937			80.0	+54.92	8.4	8.00		
302.4	+56.80	.98	.927			100.7	+52.18	8.3	8.02		
391.3	+53.94	.97	.926			119.5	+50.47	8.2	8.01		
542.8	+50.15	.96	.925			149.9	+48.66	8.2	8.07		
670.7	+47.79	.95	.924			∞	+46.34				
766.0	+46.37	.95	.927								
∞	+40.19										
Average			.930		11.9	Average			8.03		79.0

4.1 g per 100 ml at 0° C read in a 4-dm tube $^{\circ}S = -14.83\times10^{-.00926t}+1.16\times10^{-.0167t}+39.56$ $[\alpha]_D^t = {}^{\circ}S\times2.1234$						4.0 g per 100 ml at 20° C read in a 4-dm tube $^{\circ}S = -14.86\times10^{-.00813t}+2.25\times10^{-.0452t}+36.86$ $[\alpha]_D^{20} = 2.1758\times{}^{\circ}S$					
3.9	+25.81			+0.97		2.00	+24.05			+1.50	
9.3	+25.84	0.000		+.84	11.6	3.41	+24.05	0.00		+1.13	87.2
17.4	+25.82	.000		+.57	17.1	4.66	+24.14	1.15		+.90	83.4
25.3	+25.87	.089		+.39	18.4	7.51	+24.43	2.37		+.48	89.8
39.2	+26.15	.308		+.27	15.7	10.02	+24.81	3.31		+.27	92.9
50.3	+26.33	.361		+.13	18.8	20.27	+26.68	5.46		(+.10)	
59.9	+26.54	.423		+.09	18.4	30.25	+28.42	6.41			
91.4	+27.25	.549				40.18	+29.85	6.86	8.12		
119.6	+27.98	.645				49.98	+31.00	7.08	8.03		
181.6	+29.36	.730	(0.889)			59.86	+32.01	7.29	8.12		
242.4	+30.58	.776	.899			76.40	+33.30	7.47	8.12		
302.1	+31.61	.761	.895			89.83	+34.11	7.61	8.17		
369.3	+32.64	.816	.895			119.33	+35.23	7.63	8.02		
519.5	+34.50	.842	.899			149.98	+36.00	7.93	8.28		
618.3	+35.40	.845	.892			181.2	+36.40	8.06	(8.37)		
755.7	+36.47	.862	.902			∞	+36.86				
1370	+38.63	.856	(.876)								
∞	+39.56										
Average			.897		16.7	Average			8.12		88.3

TABLE 11.—*Complex mutarotations of sugars in water*—Continued

MANNOSE $CaCl_2.4H_2O$

8.4 g per 100 ml at 0° C read in a 4-dm tube $°S = 4.34\times10^{-.02674} - 39.28\times10^{-.02681} + 6.04$ $[\alpha]_D^0 = °S \times 1.0265$						9.1 g per 100 ml at 20° C read in a 2-dm tube $°S = 2.16\times10^{-.02424} - 22.13\times10^{-.3114} + 3.23$ $[\alpha]_D^{20} = °S \times 1.8576$					
Time	Observed reading	$(k_1+k_2)\times10^3$	$m_1\times10^3$	Deviation	$m_2\times10^3$	Time	Observed reading	$(k_1+k_2)\times10^3$	$m_1\times10^3$	Deviation	$m_2\times10^3$
1	2	3	4	5	6	1	2	3	4	5	6
Minutes	°S			°S		*Minutes*	°S			°S	
1.3	−22.40			−32.75		1.2	−4.12			−9.37	
3.6	−13.05			−23.33	64.0	1.8	−1.07			−6.25	293
8.2	−2.16			−12.33	61.5	2.0	−.27			−5.43	296
11.8	+2.48			−7.57	60.6	2.3	+.81			−4.32	306
20.9	+7.61			−2.25	59.3	2.6	+1.63			−3.46	309
25.3	+8.50			−1.25	59.1	2.8	+2.33			−2.74	334
29.9	+9.02			−.63	60.0	3.1	+2.73			−2.31	320
39.8	+9.29			−.15	60.8	3.4	+3.08			−1.93	312
44.7	+9.22			−.12		4.3	+3.88			−1.04	308
60.4	+8.99			−.04		4.7	+4.18			−.71	320
75.4	+8.77					7.8	+4.62				
150.5	+7.74		2.74			9.9	+4.44		(28.7)		
179.7	+7.49		2.63			13.8	+4.22		24.5		
208.5	+7.24		2.68			19.5	+3.96		23.9		
240.2	+7.06		2.59			31.2	+3.59		25.1		
300.0	+6.71		2.72			45.6	+3.33		(30.2)		
∞	+6.04					∞	+3.23				
Average			2.67		60.8	Average			24.5		311

α-d-TALOSE

4.0 g per 100 ml at 0.1° C read in a 4-dm tube $^{\circ}S = 4.49\times10^{-.003931t}+12.60\times10^{-.0345t}+11.56$ $[\alpha]_D^{0.1} = ^{\circ}S\times2.1790$						4.0 g per 100 ml at 20° C read in a 4-dm tube $^{\circ}S = 4.25\times10^{-.0253t}+17.35\times10^{-.1201t}+9.51$ $[\alpha]_D^{20} = ^{\circ}S\times2.1872$					
2.13	+27.09			+11.12		2.86	+20.65			+7.57	
6.52	+24.46	18.36		+8.65	24.9	4.42	+17.71	85.3		+4.95	118.3
15.27	+20.76	17.30		+5.25	24.8	6.57	+15.05	81.8		+2.68	121.6
25.18	+18.15	16.15		+2.95	25.0	8.92	+13.34	76.5		+1.35	123.6
30.14	+17.28	15.49		+2.23	24.9	11.85	+12.09	70.7		+.51	130.3
40.01	+15.98	14.41		+1.20	25.5	14.82	+11.42	64.0		+.18	135.8
50.13	+15.15	13.25		+0.63	26.0	17.41	+11.03	59.5		+.04	(156.5)
59.89	+14.59	12.29		+.30	27.2	20.08	+10.77	55.0			
95.27	+13.59	9.49				25.13	+10.43	48.6	27.0		
119.83	+13.22	8.25	3.56			30.08	+10.21	44.2	25.5		
180.79	+12.53	6.74	3.75			∞	+9.51				
240.86	+12.16	5.92	3.64								
305.45	+11.93	5.35	3.52								
∞	+11.56										
Average			3.62		25.5	Average			26.3		125.9

l-RIBOSE

4.1 g per 100 ml at 0.2° C read in a 4-dm tube $^{\circ}S = -3.72\times10^{-.0060t}+3.83\times10^{-.0441t}+10.98$ $[\alpha]_D^{0.2} = ^{\circ}S\times2.1129$						4.0 g per 100 ml at 20° C read in a 4-dm tube $^{\circ}S = -3.64\times10^{-.049t}+3.46\times10^{-.231t}+9.90$ $[\alpha]_D^{20} = ^{\circ}S\times2.0909$					
2.23	+10.28			+2.90		1.59	+9.27			+2.41	
3.73	+9.83			+2.36	59.7	2.22	+8.83			+1.76	217
6.82	+9.28			+1.64	53.9	2.77	+8.58			+1.34	216
9.87	+8.95			+1.15	52.6	3.33	+8.36			+.96	230
14.91	+8.71			+.67	50.2	4.44	+8.18			+.48	246
19.80	+8.67			+.40	48.7	5.78	+8.22			+.21	248
25.11	+8.64			+.16	55.0	7.38	+8.39			+.07	
30.37	+8.76			+.08	55.4	8.76	+8.59			+.04	
40.08	+9.01					9.90	+8.71				
60.07	+9.58		7.42			13.68	+9.10		45.6		
75.51	+9.85		6.81			17.33	+9.39		49.5		
89.77	+10.08		6.85			20.48	+9.55		50.2		
104.99	+10.28		6.92			25.08	+9.70		51.0		
120.19	+10.46		7.22			29.88	+9.78		49.9		
151.45	+10.61		6.52			∞	+9.90				
181.15	+10.73		6.36								
∞	+10.93										
Average			6.87		53.6	Average			49.2		231

The thermal mutarotations were conducted in the following manner: The sugar solution in a 4-dm water-jacketed silver tube was allowed to reach equilibrium at 25° C, and its optical rotation read. The water (at 25° C) was drained from the water jacket and a stream of aqueous alcohol cooled to 0° C was pumped through the jacket. Time was measured from the moment when the cold aqueous alcohol was turned on. The temperature dropped in about 3 minutes to approximately 0° C, at which time saccharimeter readings were made. The calculation of the results is described on page 156.

TABLE 12.—*Thermal mutarotations*

Thermal mutarotation of a 10-percent aqueous solution of *d*-galactose after cooling from 25 to 0.3° C. $°S = 1.10 \times 10^{-.001071} - 3.49 \times 10^{-.01324} + 97.87$.

Time*	Saccharimeter reading	$m_1 \times 10^3$	Deviation	$m_2 \times 10^3$
Minutes	°S		°S	
5.74	+96.02		−2.93	
6.95	+96.13		−2.82	13.8
10.00	+96.49		−2.45	18.2
15.13	+96.74		−2.19	13.5
20.09	+97.04		−1.88	13.4
26.15	+97.32		−1.58	13.1
30.20	+97.46		−1.43	12.7
40.27	+97.76		−1.10	12.3
50.11	+98.02		−0.82	12.5
60.96	+98.23		−.59	12.6
75.23	+98.41		−.37	12.9
89.97	+98.48		−.27	12.3
126.54	+98.53		−.14	10.9
139.88	+98.60		−.05	13.2
160.18	+98.61			
244.19	+98.45	1.26		
306.1	+98.39	1.05		
365.2	+98.30	1.15		
502.1	+98.24	0.88		
738.7	+98.06	1.02		
∞	+97.87			
Average		1.07		13.2

Thermal mutarotation of an 8-per cent aqueous solution of *l*-arabinose after cooling from 25.2 to 0.2° C. $°S = 1.52 \times 10^{-.003441} - 4.56 \times 10^{-.02713} + 101.71$

4.57	+99.74		−3.43	
5.94	+100.01		−3.15	27.0
8.29	+100.38		−2.75	25.8
10.64	+100.75		−2.35	27.1
15.16	+101.30		−1.75	27.6
20.21	+101.71		−1.28	27.4
25.58	+102.01		−.93	27.0
30.06	+102.20		−.69	27.3
40.10	+102.45		−.35	27.9
51.15	+102.55		−.12	(31.3)
75.14	+102.52			
90.19	+102.41	4.21		
121.06	+102.26	3.66		
154.66	+102.11	3.85		
184.1	+102.06	3.34		
214.6	+101.98	3.42		
277.9	+101.87	3.47		
330.6	+101.81	3.56		
389.9	+101.77	3.59		
∞	+101.71			
Average		3.64		27.1

* Time is measured from the beginning of the cooling process.

TABLE 12.—*Thermal mutarotations*—Continued

Thermal mutarotation of an 8-percent aqueous solution of *d*-talose after cooling from 25.8 to 0.1°C. $°S = 0.14 \times 10^{-.0036t} - 4.69 \times 10^{-.0391t} + 23.62$

Time	Saccharimeter reading	$m_1 \times 10^3$	Deviation	$m_2 \times 10^3$
Minutes	°S		°S	
3.94	+20.14	----------	−3.61	----------
5.41	+20.57	----------	−3.18	(37.5)
7.42	+20.93	----------	−2.82	30.8
10.24	+21.35	----------	−2.39	28.4
13.55	+21.84	----------	−1.90	29.0
16.85	+22.15	----------	−1.59	27.6
19.97	+22.40	----------	−1.33	27.0
24.98	+22.76	----------	−.97	27.1
29.92	+23.10	----------	−.63	29.2
39.98	+23.45	----------	−.27	31.2
50.07	+23.56	----------	−.15	29.9
60.09	+23.61	----------	−.09	28.6
96.3	+23.68	[b](3.8)	----------	----------
∞	+23.62	----------	----------	----------
Average	----------	----------	----------	28.9

[b] The mutarotation due to the slow reaction is scarcely more than the experimental error and, therefore, the value of m_1 (.0036) obtained from the mutarotation of α-*d*-talose was used for extrapolating the slow reaction back to zero time. The existence of the maximum was shown by comparing the average of a large number of readings at about 90 minutes with the average of similar readings after equilibrium was established. Several duplicate experiments revealed a difference of about 0.08° S, which corresponds to a total change of 0.14° S.

Because of the general applicability to experiments requiring a continuous flow of cold water at a constant temperature, the apparatus used for the low-temperature measurements will be described, although the general methods involved are not new. A copper tank of 40 gallons capacity was placed inside a standard electric refrigerator (10 ft.^{3} capacity) in such a manner that the cooling coils dipped about 10 inches into the tank. An outlet at the bottom of the tank allowed liquid to flow into a standard centrifugal pump (operated by a ¼ hp motor) which circulated the cooling medium. Instead of passing the liquid through the jacket of the polariscope tube, the major portion was bypassed so as to allow the pump to operate at full capacity. The return flow was led through the back of the refrigerator and split into two streams which were discharged over the upper shelves of the two cooling coils. The temperature was held constant by use of a mercury thermoregulator. The most satisfactory cooling medium was found to be 95-percent ethyl alcohol. The advantages of the alcohol over aqueous solutions containing but little alcohol are (1) the lower specific heat of the alcohol allows more rapid cooling of the liquid to the desired temperature, a quicker establishment of a constant temperature in the circulating water after the pump is started, and a lower operating temperature; and (2) the alcohol reduces corrosion. The apparatus described was found quite satisfactory for the mutarotation measurement at 0° C. Polariscope tubes were kept at a constant temperature of 0±0.03° C for a week at a time.

V. SUMMARY

Fundamental characteristics of the alpha and beta sugars which furnish the basis for the changes in nomenclature previously suggested by Isbell are discussed, and it is shown that the sugars which appear

as beta modifications under the proposed classification are oxidized by bromine more rapidly than the alpha isomers.

The oxidation of the equilibrium solutions of the sugars proceeds rapidly until a part of the sugar is used up and then more slowly as the remaining sugar continues to be oxidized. The oxidation of the more reactive fractions takes place at rates comparable to those found for the beta sugars, while the rates for the less reactive fractions agree within reasonable experimental error with the rates for the oxidation of the alpha sugars. The proportions of the more rapidly and the less rapidly oxidizable sugars were determined and compared with the proportions of the alpha and beta isomers calculated from the optical rotations on the assumption that the equilibrium solutions contain only the alpha and beta normal isomers. The results of these comparisons indicate that the equilibrium solutions are principally of the normal alpha and beta sugars, but the presence of small quantities of other modifications is not excluded, especially for the solutions of galactose, arabinose, talose, and ribose. The oxidation of equilibrium solutions of *l*-ribose has revealed that they contain a small quantity of some modification which is more easily oxidizable than the crystalline sugar which was previously classified as *β-l*-ribose. The existence of this easily oxidizable modification throws doubt on the correctness of the classification of the known sugar as the beta form. The oxidation of (*d*-gulose)$_2$ $CaCl_2$. H_2O shows that the crystalline sugar contains about 32 percent of an easily oxidizable modification which is presumably the heretofore unknown beta isomer.

Mutarotation measurements at 20° C and at 0° C reveal that the mutarotations of *α*- and *β-d*-glucose, *α*- and *β-d*-mannose, *α-d*-gulose $CaCl_2.H_2O$, (*d*-gulose)$_2$ $CaCl_2.H_2O$, *α*- and *β-d*-lyxose, *α-d*-xylose, *α-l*-rhamnose (hydrate), *α*- and *β*-lactose, and *β*-maltose follow the first-order equation, while the mutarotations of *α*- and *β-d*-galactose, *α-l*-arabinose, *β-l*-arabinose $CaCl_2.4H_2O$, *d*-mannose $CaCl_2.4H_2O$, *α-d*-talose, and *l*-ribose are complex. The initial and equilibrium specific rotations of these sugars were determined at 0 and 20° C, and values for the rotation of the first carbon (Hudson's *A*) were calculated at both temperatures. The effect of traces of heavy metals on the rates of mutarotation is pointed out and attention is directed to errors caused by the use of nickel-plated brass tubes in mutarotation measurements. The optical rotations of mannose $CaCl_2.4H_2O$ and arabinose $CaCl_2.4H_2O$ are reduced to equations containing two exponential terms, and attention is directed to the fact that the addition of calcium chloride produces a change in the equilibrium between the various modifications of these sugars in solution. Detailed data for the optical rotations of *α-d*-talose at 20° C and at 0° C are reported for the first time.

Temperature coefficients were determined for the mutarotations of 20 sugars. The principal mutarotation reactions (supposedly the reversible interconversion of the normal alpha and beta isomers) are on the average 8.34 times as fast at 20° C as at 0° C, while the rapid reactions are on the average only 5.32 times as fast at 20° C as at 0° C. The higher temperature coefficient for the principal mutarotation reaction shows that the heat of activation is greater for the interconversion of the normal isomers than for the rapid reaction. The mutarotations which occur after a sudden change in temperature prove that the compositions of equilibrium solutions of galactose, arabinose, and talose are altered markedly by a change in temperature. The pro-

portions of the labile constituents vary with temperature more than the proportions of the normal alpha and beta isomers. In this respect it is shown that the bromine oxidation of solutions of *d*-galactose in equilibrium at 20° C does not differ widely from the oxidation of solutions in equilibrium at 0° C.

The optical rotation of a freshly prepared solution containing α- and β-*d*-galactose in proportions corresponding to the equilibrium rotation decreases to a minimum and then increases to the original value. This is conclusive proof that the deviations in the mutarotations of α- and β-*d*-galactose are real.

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EFFECT OF TEMPERATURE ON THE STRESS-DEFORMATION OF CONCRETE

By Arthur U. Theuer

ABSTRACT

A number of important investigations have provided information relative to the elastic and plastic properties of concrete. In order to obtain additional information on these properties, a series of tests were made to determine the effect of change of temperatures within the range 26 to 123° F on the elastic and plastic deformations of portland cement concrete when subjected to sustained compressive stress. Tests were made on concretes of two greatly different strengths and under three conditions of moisture content. The specimens were subjected to sustained compressive stress for periods of 3 days, deformation readings being taken both immediately before and after loading, at intervals during the 3-day period of loading, immediately after unloading, and thereafter at intervals during the 3-day period following unloading. For all tests the applied stress was held at an estimated 20 percent of the strength of the specimens. Characteristic trends of the elastic and plastic behavior of the concretes were determined.

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I. INTRODUCTION

Several important investigations [1] have provided information on the elastic and plastic properties of hardened portland cement concretes. In order to determine the effect of temperature on these properties, the tests described in this paper were undertaken. Two concretes, differing greatly in strength, were subjected for 3 days to sustained compressive stresses estimated at approximately 20 percent of their ultimate strength. During the period while under load, and for a period of 3 days following the release of load, deformation readings were taken at regular time intervals. The specimens were maintained during a test at a constant temperature within the range 26 to 123° F, and in one of three moisture conditions, namely, saturated, partially dry, or oven dry.

[1] See, for example, R. E. Davis, et al., *Plastic flow of concrete under sustained stress*, Proc. Am. Soc. Testing Materials 34 II, 354 (1934); W. H. Glanville, *The creep or flow of concrete under load*, Tech. Pap. 12, British Building Research Board (London), and bibliographies in Proc. Am. Soc. Testing Materials 30 I, 635 and 661 (1930), and 28 II, 337 (1928).

II. APPARATUS

Details of the loading apparatus,[2] as well as the method of mounting the gages and of sealing the concrete cylinders in rubber tubing

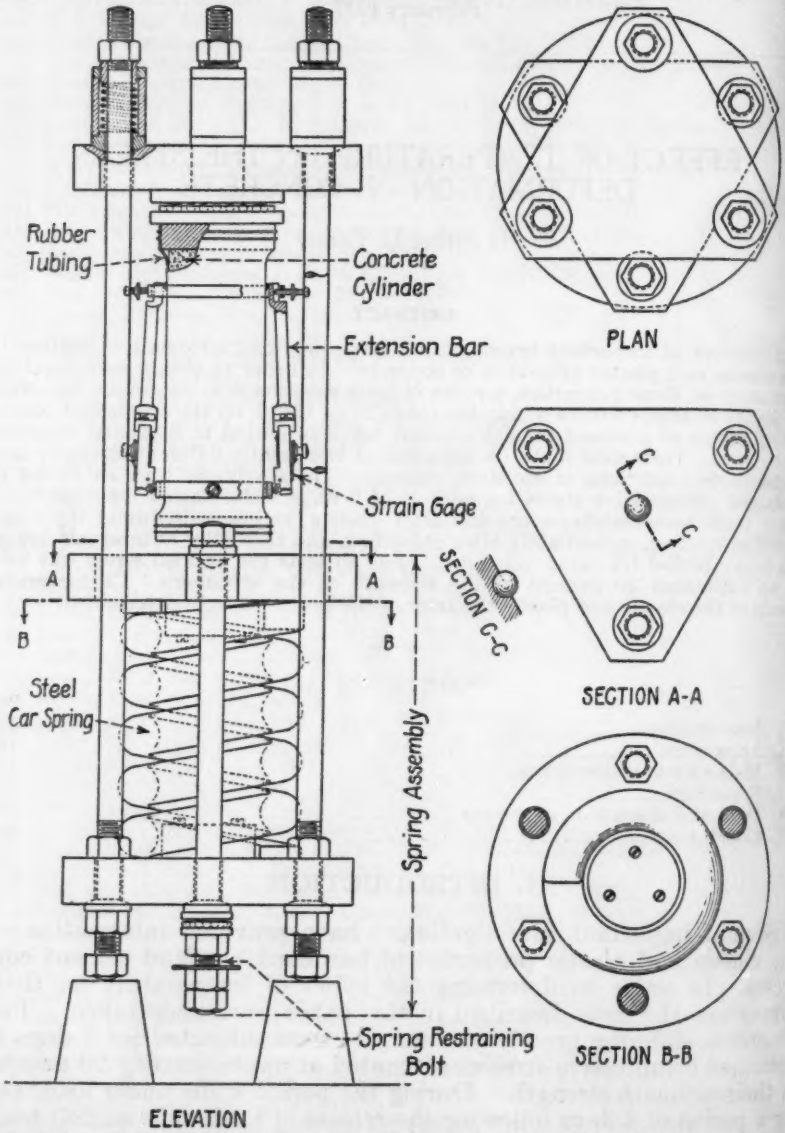

FIGURE 1.—*Loading apparatus assembled for test with specimen in place and gages mounted.*

to reduce, as far as possible, changes in moisture content, are illustrated in figure 1.

The spring assemblies were calibrated in a beam type of testing machine. The relation between load and length of spring was first

[2] The loading apparatus was designed by Dr. S. Springer, of Budapest, Hungary, while at the National Bureau of Standards.

determined in a series of preliminary tests. This relation was also determined before and after each test. The data obtained indicated that the spring loads as applied to the concrete cylinders could be determined to within an accuracy of 0.5 percent.

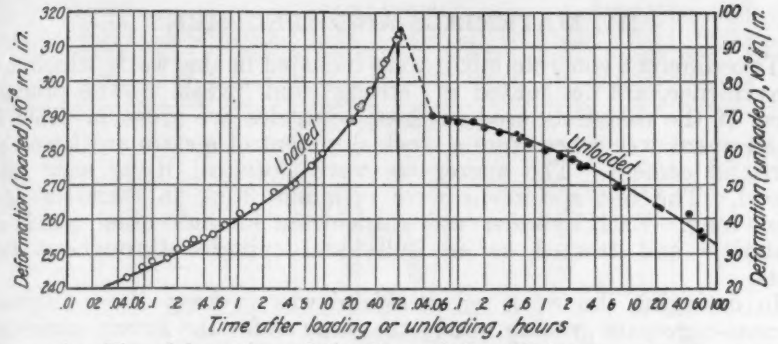

FIGURE 2.—*Time-deformation relation for cylinder 2W (strong saturated concrete) representing a complete loading and unloading cycle.*

This graph was plotted through points taken from the original test data. The zero deformation point is the gage reading immediately before the application of load.

Deformations of the concrete cylinders were measured by means of Tuckerman optical strain gages and autocollimator.[3]

The fixed ends of the gages rested on small aluminum plates placed directly against the cylinder. The other ends of the gages rested on

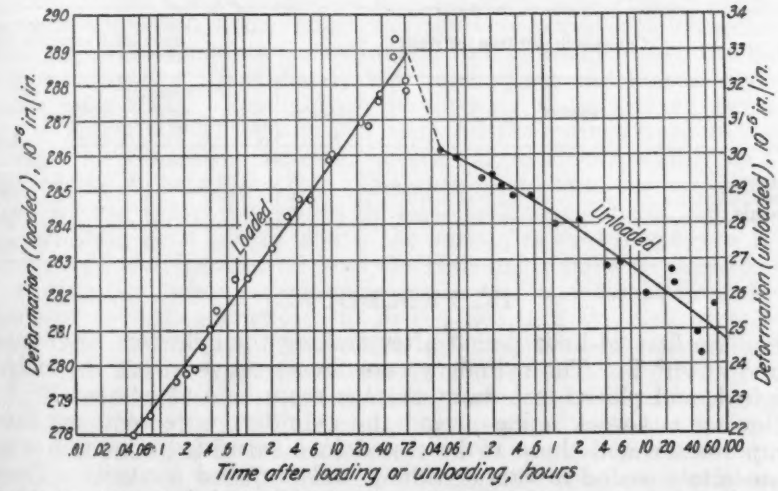

FIGURE 3.—*Time-deformation relation for cylinder 7D (strong dry concrete) representing a complete loading and unloading cycle.*

This graph was plotted through points taken from the original test data. The zero deformation point is the gage reading immediately before the application of load.

a collar fixed to the cylinder by means of three setscrews bearing against small aluminum plates. These gages may be read directly to 2×10^{-6} in./in. in a 2-in. gage length. This degree of accuracy could not be obtained, however, in the tests owing to small rapid fluctuations in the temperature of the surrounding air with the

[3] For a description of these gages see Proc. Am. Soc. Testing Materials **23**, II, 602 (1923).

resulting effect of varying the lengths of the gages almost instantaneously and the concrete scarcely at all. The accuracy of a single reading is very near to $\pm 5 \times 10^{-6}$ in./in. The accuracy of the observations may be judged by the two curves, figures 2 and 3.

III. MATERIALS AND SPECIMENS

Two different concrete mixes were included in this work, which, for convenience, are designated as "strong" and "weak." The proportions of the materials used in these concretes are given in table 1. The cement was taken from a stock shipment of a standard brand of portland cement. The aggregates were Potomac River sand and gravel. The test specimens were cylinders 3 in. in diameter and 8 in. long. Each cylinder was made from an individual batch of materials and treated as an individual cylinder throughout the tests.

In designing the weak mix the aim was to keep the combined cement-aggregate grading nearly the same as for the strong concrete, a decrease in strength being secured by replacing a certain amount of the cement by aggregate while still retaining the desirable workability and uniformity in finished product.

The concretes were mixed by hand for a period of 4 minutes, and were placed in the molds in four layers, each layer being rodded 50 times. The molds were designed to be practically watertight to keep evaporation losses to a minimum.

TABLE 1.—*Concrete and aggregate*

Concrete proportions (by weight)			Grading of combined cement and aggregate (by absolute volume)		
Ingredients	Strong	Weak	Passed sieve no.—	Strong	Weak
			Inch		
Cement	1.00	1.00	¾	100.0	100.0
Water	.40	.80	4	73.2	75.6
Aggregate	3.00	6.37	8	62.5	62.0
			16	53.5	53.0
			50	32.1	30.3

IV. PROCEDURE

For the first 24-hour period after making the cylinders, they were stored at 70° F. The cylinders were then removed from the molds, weighed, and placed in a damp-storage room held at or near 70° F.[4] Following a 4-week aging period the cylinders were removed from damp storage and those to be tested in a saturated condition were immediately sealed in rubber tubing and prepared for tests. Those to be tested dry were placed for a period of 1 week in an oven held at 230° F, before being sealed for test; and those to be tested in a semidry condition were placed in an oven held at 104° F until their loss of moisture fell within the ranges 22 to 37 and 50 to 70 percent, respectively, of the loss of the strong and weak cylinders dried at 230° F before being sealed for test. The cylinders dried at 230° F are designated hereafter as "dry", and those dried at 104° F as "semidry." All data pertaining to moisture losses and gains are included in table 2.

[4] Temperatures 8 to 10° F below normal were recorded in the damp-storage room for nearly a week each, on two occasions. A part of the variation in the strength of certain of the test cylinders is believed to be caused by this difference in storage temperature.

TABLE 2.—*Percentage weight loss or gain in moisture during the time the test specimens were being cured, dried, and under test*

[All values for gain or loss are percentages of water content at start of exposure]

Wet			Dry				Semidry			
Cylinder no.	Gain in weight during 4 weeks of curing	Loss in weight during test	Cylinder no.	Gain in weight during 4 weeks of curing	Loss in weight on drying 1 week at 230° F	Gain in weight during test	Cylinder no.	Gain in weight during 4 weeks of curing	Loss in weight on drying at 104° F	Gain in weight during test
STRONG CONCRETE										
1W	−1.7	1.0	7D	7.3	66.3	2.0	15SD	5.6	22.6	−0.9
2W	−2.0	1.0	8D	7.3	66.8	1.4	16SD	7.8	19.9	−.8
3W	.5	4.9	9D	4.1	65.6	7.5	17SD	8.3	15.3	.5
4W	.5	4.9	10D	2.4	64.7	6.5	18SD	8.3	15.5	.0
5W	4.6	1.2	11D	5.4	67.1	.0	19SD	4.6	23.8	.0
6W	4.4	1.2	12D	6.8	69.4	.7	20SD	5.1	23.9	.6
			13D	5.4	64.8	.0	21SD	6.3	14.9	−.8
			14D	6.8	70.3		22SD	6.8	16.5	−.5
							23SD	6.8	15.7	−.5
WEAK CONCRETE										
24W	7.0	0.7	34D	3.0	77.7	2.0	44SD	6.5	43.5	−1.5
25W	6.7	.7	35D	3.7	78.0	1.0	45SD	6.5	41.5	−.7
26W	6.7	.0	36D	.0	74.4	3.6	46SD	6.3	51.6	−.9
27W	7.0	.4	37D	.0	80.0	8.1	47SD	6.5	49.3	.0
28W	−2.3	5.0	38D	6.1	77.4	1.0	48SD	4.4	43.8	−.8
29W	−2.6	4.8	39D	6.3	76.1	1.8				
30W	.0	.0	40D	5.4	74.6	2.6				
31W	.9	.0	41D	5.6	72.9	1.6				
32W	7.7	5.2	42D	.7	84.0	4.4				
33W	6.7	5.0	43D	1.6	82.8	9.3				

The cylinders were subjected to a sustained compressive stress for a period of 3 days; deformation readings were taken both immediately before and after loading the cylinders, at intervals through the 3-day period of loading, immediately after unloading, and thereafter for a period of 3 days. The method of applying the sustained stress to the cylinders was as follows: For each test the springs were first compressed in the testing machine under a load corresponding to that desired for a particular test. The spring was then secured between the two end plates by means of three restraining bolts. After the cylinder had been placed above the spring, as shown in figure 1, the spring load was transferred from the restraining bolts to the cylinder.

During the 6-day period while under test and for at least 1 day previous to the commencement of the test, the cylinders were kept at as nearly a uniform temperature and moisture content as possible. Variations in the moisture content during the tests are given in table 2, and variations in temperature during the test are given as maximum deviations in table 3. Uniform temperature of concrete during the tests was obtained by resort to constant-temperature rooms and uniform moisture content by means of sealing the concrete specimens in rubber bags (fig. 1).

In order to obtain a measure of the deformations caused by temperature and shrinkage changes, deformation readings were always taken on an unloaded cylinder at the same time that readings were taken on the loaded cylinders. The magnitude of the deformations occurring on the unloaded cylinders and applied as a correction to the data for the loaded cylinder averaged about 5×10^{-6} in./in., with 12×10^{-6} in./in. as a rather extreme value. Differential effects between the steel gages and concrete specimens with relatively rapid temperature changes usually constituted a major portion of these changes.

TABLE 3.—*Deformation values at six successive intervals after loading and unloading*

W, specimens tested as taken from damp storage.
D, specimens dried at 230° F.
SD, specimens dried at 104° F.

Cylinder no.	Compressive strength at 42 days f_c	Stress σ	Ratio, stress to strength σ/f_c	Temperature		Total deformations in 10^{-6} in./in. at time, t, after												Residual deformation
				Average T	Maximum deviation R	Loaded (total deformation)						Unloaded (recovery)						
						0.05 hr	0.2 hr	1 hr	6 hr	24 hr	72 hr	0.05 hr	0.2 hr	1 hr	6 hr	24 hr	72 hr	
				STRONG CONCRETE														
	lb/in²	lb/in²		° F	° F													
1*W*	6,040	1,125	0.1862	72	1.6	253	259	269	290	306	318	246	252	257	270	279	285	33
2*W*	6,080	1,128	.1856	------	------	243	250	260	273	290	312	242	247	252	263	272	279	33
3*W*	6,610	1,124	.1700	125	1.4	255	267	278	305	345	377	203	205	208	220	241	265	112
4*W*[a]	------	------	------	------	------	----	----	----	----	----	----	----	----	----	----	----	----	----
5*W*	5,880	1,123	.1910	43	1.8	242	248	256	271	281	288	237	240	247	256	260	264	24
6*W*	5,870	1,120	.1909	------	------	245	251	259	275	283	291	240	243	250	259	264	267	24
7*D*	6,970	1,128	.1618	73	1.4	278	280	282	285	287	289	259	260	261	262	263	264	25
8*D*	6,380	1,128	.1767	------	------	304	306	310	314	316	317	299	300	302	303	303	303	14
9*D*	6,530	1,128	.1726	123	1.4	310	318	323	328	329	332	310	311	314	316	317	319	13
10*D*	6,300	1,128	.1790	------	------	318	328	334	336	337	339	324	325	330	333	334	235	4
11*D*	5,830	1,128	.1935	49	2.9	325	329	331	334	336	337	310	312	313	315	317	319	18
12*D*	5,770	1,124	.1948	------	------	317	320	322	325	327	328	292	294	295	297	298	299	29
13*D*	6,390	1,125	.1761	40	4.5	310	313	317	320	322	323	293	294	296	297	298	299	24
14*D*	6,730	1,128	.1675	------	------	308	310	314	317	320	321	289	290	291	293	294	295	26
15*SD*	7,090	1,130	.1594	104.5	1.8	285	293	308	330	364	399	252	257	266	276	287	298	101
16*SD*	7,050	1,125	.1596	------	------	288	296	310	333	366	402	256	260	268	278	290	301	101
17*SD*	6,990	1,128	.1614	58.5	1.5	290	297	305	318	334	354	262	267	273	280	286	291	63
18*SD*	7,090	1,124	.1586	------	------	292	300	308	322	338	357	264	268	274	281	288	295	62
19*SD*	7,120	1,128	.1584	102	4.5	311	321	330	354	384	421	266	274	280	292	302	313	108
20*SD*	7,050	1,122	.1591	------	------	299	311	320	344	372	408	265	272	277	288	299	310	98
21*SD*	7,140	1,130	.1583	86.5	.5	278	290	303	324	351	381	242	248	254	263	274	284	97
22*SD*	7,780	1,130	.1452	40.5	1.0	266	273	280	294	310	329	244	249	254	261	267	273	56
23*SD*	7,470	1,130	.1513	------	------	252	259	264	276	291	307	234	239	243	250	256	262	45
				WEAK CONCRETE														
24*W*	2,650	432	0.1630	72	1.3	118	121	126	135	142	148	115	117	120	126	130	134	14
25*W*	2,740	435	.1587	------	------	119	122	128	137	144	150	114	115	118	124	128	132	18
26*W*	2,520	592	.2350	72	1.9	168	173	179	192	202	210	162	164	170	179	183	186	24
27*W*	2,650	589	.2222	------	------	164	168	174	188	198	206	159	162	167	175	180	183	23
28*W*	3,040	591	.1945	122	2.2	167	178	190	227	256	280	----	170	171	----	----	198	82
29*W*	3,080	592	.1922	------	------	172	184	199	236	264	287	----	182	184	----	----	214	73
30*W*	2,370	591	.2494	56	5.2	164	169	176	190	200	207	150	161	166	173	179	182	25
31*W*	2,560	580	.2266	------	------	156	160	167	180	188	195	153	156	160	167	172	175	20
32*W*	2,630	592	.2250	96	1.8	178	186	197	213	232	255	168	172	179	187	197	204	51
33*W*	2,620	590	.2253	------	------	180	188	198	215	234	262	185	190	195	204	213	220	42
34*D*	2,850	584	.2050	72	1.1	242	243	246	250	252	253	214	216	218	221	222	223	30
35*D*	2,850	591	.2074	------	------	233	236	240	244	246	247	209	210	212	215	216	218	29
36*D*	2,920	582	.1994	122	1.8	216	218	226	230	231	232	201	203	207	210	211	212	20
37*D*	2,720	591	.2172	------	------	248	250	255	259	261	262	228	229	231	235	237	238	24
38*D*	2,740	590	.2153	26	6.0	222	224	226	230	232	234	198	199	201	204	205	205	29
39*D*	2,700	592	.2193	------	------	225	228	231	234	237	238	207	208	210	212	213	214	24
40*D*	2,420	587	.2427	41	2.0	256	257	260	264	266	268	223	224	227	230	231	232	36
41*D*	2,760	590	.2138	------	------	236	237	240	244	246	248	206	208	212	214	215	216	32
42*D*	2,550	594	.2330	95	2.6	259	263	266	270	273	276	235	237	238	240	242	244	32
43*D*	2,630	590	.2243	------	------	250	253	256	259	261	264	214	216	218	220	221	222	42
44*SD*	3,110	590	.1898	105	2.7	193	199	212	233	261	297	184	190	196	205	215	226	71
45*SD*	3,230	592	.1833	------	------	181	188	201	223	254	293	169	172	178	186	198	206	87
46*SD*	2,910	590	.2027	44	.8	197	200	202	206	209	212	180	181	183	184	186	188	24
47*SD*	3,090	590	.1910	------	------	188	190	193	195	197	199	174	175	177	179	181	182	17
48*SD*	3,090	590	.1910	86	.5	184	193	200	217	240	270	168	174	178	184	191	198	72

[a] Bag broken during test.

After completion of the load-deformation test the cylinders were stored in a sealed condition at a temperature of 70° F until tested for compressive strength at the age of 6 weeks.

V. DATA AND DISCUSSION OF RESULTS

Data on the compressive strength of the cylinders, stress and temperature of the concrete during the load tests, and deformation values of the specimens at six successive intervals of time after loading and unloading are given in table 3. All deformation values given in this table, excepting the deformation value at the 0.05-hour interval, have been taken from smooth curves drawn through points plotted from the original test data (corrected for shrinkage and temperature changes, as indicated by the readings on the unloaded cylinder). The original test data usually included 20 or more time-deformation observations. Two representative curves of this type, plotted with semilogarithmic coordinates, are included as figures 2 and 3. The

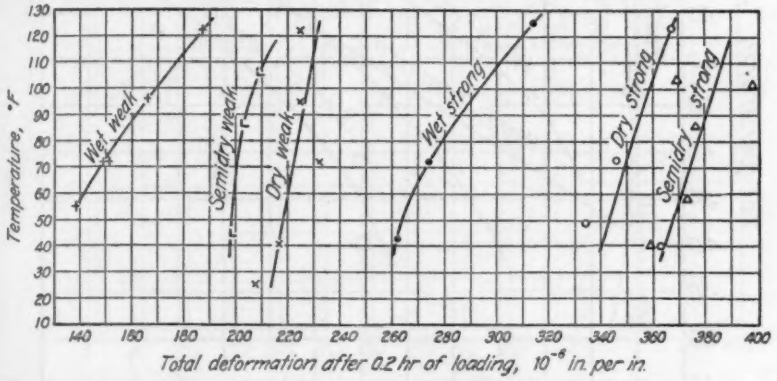

FIGURE 4.—*Relation between the total deformation at 0.2 hour after the application of load and the temperature of the concrete.*

Plotted points represent the average of the adjusted observations made on two cylinders tested simultaneously. The adjustment was made by multiplying the deformations by the factor $\frac{0.2 f_c}{\sigma}$.

values for the deformations under load given in table 3 were taken directly from such curves; those for deformations after unloading are the differences between the total deformations immediately before unloading and the residuals shown by the curves. The data of the table give, therefore, the compressive deformations at various periods after loading and the amounts of the recoveries at the same periods after unloading.

The temperature-deformation relations for three arbitrarily defined deformations are represented in figures 4, 5, and 6. The three deformations represented are as follows: The instantaneous deformation or that part of the total deformation which occurs within 0.2 hour after application of load (fig. 4); the time deformation or that part of the total deformation that occurs in the interval 0.2 to 72 hours of sustained loading (fig. 5); and finally, the residual deformation, which is the total deformation that occurs after 72 hours of sustained loading minus the recovery that has taken place within 72 hours after release of load (fig. 6). The plotted points in these three figures represent the adjusted averages for the observations made on two cylinders

tested simultaneously. The adjustment was made on the assumption that for small differences in strength, the deformation value will be proportional to the ratio of stress to strength, and for the tests considered, is an estimate of the deformation which would have occurred if the stress upon loading had been 0.2 of the compressive strength of the concrete.

The data of table 3 and figure 4 for deformations at 0.2 hour show that the instantaneous deformations for the wet concrete were less than for dry or semidry concrete and that they increased with an increase in temperature. These deformations were greater for the dry cylinders

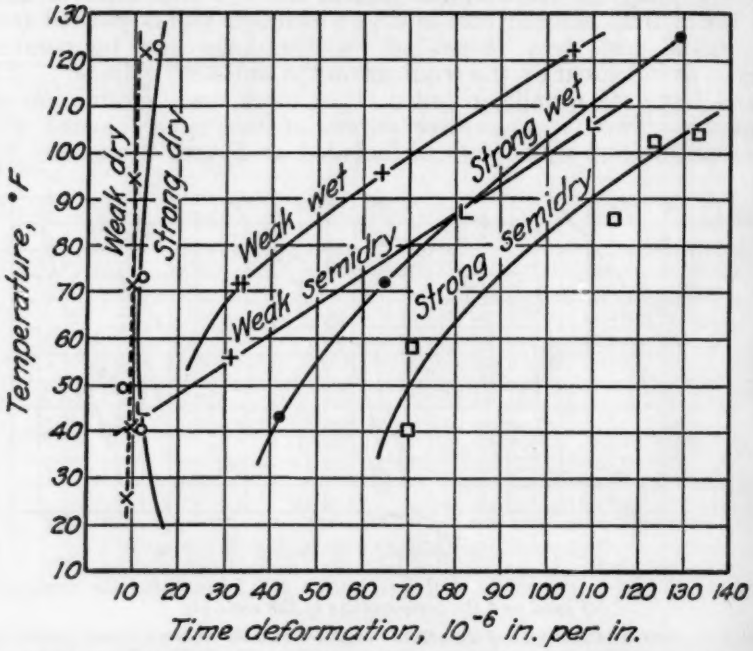

FIGURE 5.—*Relation between time deformation and temperature of concrete.*

The time deformation is that part of the total deformation occurring between 0.2 and 72 hours after the application of the test load. The plotted points represent the average of the adjusted observations made on two cylinders tested simultaneously. The adjustment was made by multiplying the deformations by the factor $\frac{0.2 f_c}{\sigma}$.

than for the semidry ones of weak concrete, whereas they were greater for the semidry than for the dry cylinders of strong concrete. However, as the time-deformation graphs showed that the rate of compression under constant load was much greater (except at the lowest temperatures used) for the semidry than for the dry concrete, it is possible that the deformations at the instant of loading for the dry strong concrete (except at the lowest temperatures) were as large as for the semidry concrete. They show also that the instantaneous deformations were larger for the strong than for the weak concretes when the compressive stresses were equal to 0.2 of the compressive strength.

As shown by figure 5, the time deformation of the oven-dried concretes was small and did not differ significantly at the various temperatures, whereas the time deformation of the wet and semidry concretes

was greater the greater the temperature of the concrete, and was greater for the strong than for the weak concrete.

The relation between the residual deformation and the test temperatures for the two concretes under three conditions of moisture content are shown in figure 6. For both concretes when dry the residual deformations are small and very nearly independent of the test temperatures. In the semidry and saturated conditions the residual deformations for both concretes increase rapidly when tested at

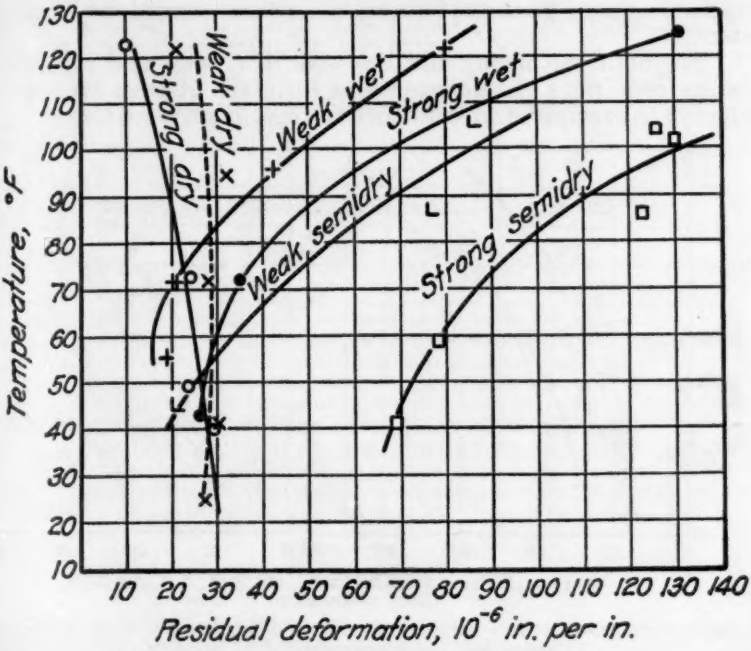

FIGURE 6.—*Relation between the residual deformation and the temperature of the concrete.*

The residual deformation is the total deformation occurring after 72 hours of sustained loading minus the recovery that has taken place within 72 hours after the release of load. The plotted points represent the average of the adjusted observations made on two cylinders tested simultaneously. The adjustment was made by multiplying the deformations by the factor $\frac{0.2 f_c}{\sigma}$.

successively higher temperatures, and was greater for the strong than for the weak concrete.

The magnitude of the residual deformations of the wet and the semidry concretes appeared to be related to the total deformation at 72 hours after loading. This is indicated by the data of figure 7, which show also that the ratio of residual deformation to the total deformation increased with an increase of temperature, but was approximately the same for the weak as for the strong concretes when each was stressed to a value equal to 0.2 the compressive strength.

Neither the deformations under load nor the recoveries after unloading showed a consistent relation with the moisture content of the concrete. As noted previously, the total deformation, the time deformation, and the residual deformation were larger for the semidry than for the wet concretes, but for the dry concretes they were not

consistently larger or smaller than for either of the others. The exposure of the dry concrete to a temperature of 230° F for 1 week may have caused changes which would not have occurred in concretes dried at a lower temperature.

VI. CONCLUSIONS

The following conclusions are drawn only with reference to the two concretes of greatly different strength which were tested over the temperature range 26 to 123° F and under three conditions of moisture content.

(1) For both the strong and the weak concretes and for all three moisture conditions the deformations for given stresses were greater the higher the temperatures at which the specimens were tested.

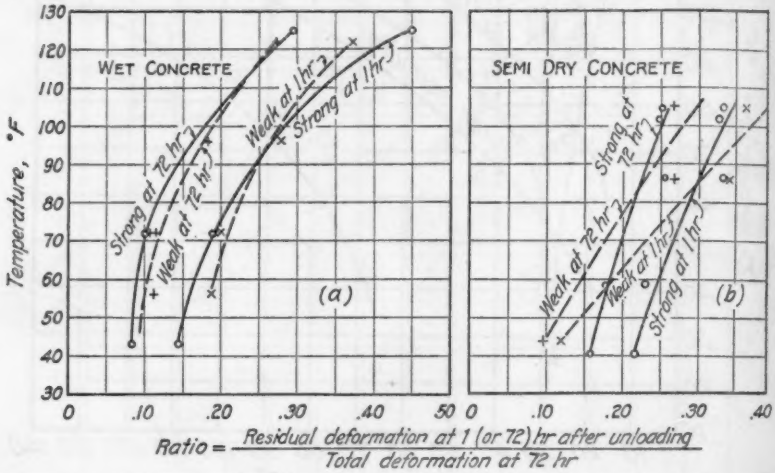

FIGURE 7.—*Relations between the ratio of residual deformation to total deformation at 72 hours, and the temperature of the concrete.*

The plotted points and curves show the values for the ratios of residual deformations (both at 1 and 72 hours after release of load) to the total deformation at 72 hours.

(2) For both concretes, when in a saturated or semidry condition, the time deformations as well as the residual deformations were greater the higher the temperature of the concrete.

(3) For both concretes in an oven-dry condition, the time deformation was relatively small and practically the same at all test temperatures.

(4) For both concretes in the dry condition, the residual deformations were small and very nearly independent of the temperature of the concrete.

(5) The instantaneous deformations of the wet concretes were less than those of the dry or semidry concretes.

(6) For the constant ratio of stress to strength of concrete, the deformations and recoveries at all periods after loading were greater for the strong than for the weak concrete when saturated or semidry; when dry, the instantaneous deformation on loading and that upon unloading likewise were greater for the strong concrete but the time deformations, recoveries, and residuals were nearly equal.

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ACCURATE REPRESENTATION OF THE REFRACTIVITY AND DENSITY OF DISTILLED WATER AS A FUNCTION OF TEMPERATURE

By Leroy W. Tilton and John K. Taylor

ABSTRACT

For a given wave length, an equation of the form

$$n_t - n_{20} = -\frac{\overline{B}(t-20)^3 + \overline{A}(t-20)^2 + \overline{C}(t-20)}{(t+\overline{D})\times 10^7},$$

an adaptation of the type of equation used by Thiesen for representing data on the density of water, has been compared with four- and six-parameter polynomials in t as a means for expressing thermal variations in the refractivity of water. All adjustments were made by the method of least squares with a precision of a few parts per million. This type of equation has also been fitted to the data obtained by Chappuis on the density of water at the International Bureau of Weights and Measures in 1891 and 1897. It fits them better than do his tabulated values. All results are examined statistically, a revised table of the density of water is given, and it is concluded that this type of equation is superior to a power series for representing either the refractive index or the density of distilled water.

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I. DISCUSSION OF FUNCTION-t EQUATIONS

For any given wave length, observed values of refractive indices may be conveniently adjusted after they have been approximately expressed as functions of the temperature, t, by what may be called function-t equations. Such functions of t are customarily polynomials in powers of t. It is well known that such equations are, in general, not desirably accurate when limited to a few terms. Moreover, Hall and Payne [1] have expressed the opinion that a single equation of this sort is not valid for a temperature range from 0 to 100° C. It seems, however, that no other type of direct [2] relationship between index and temperature has been published.

[1] Phys. Rev. [2] **20**, 249 (1922).

[2] E. Kettler (Ann. Physik **269**, 512 (1888)) used an equation that involves density as well as temperature. Regardless of its possible merit, both his sets of computed values show systematic failure to represent his data.

Under these circumstances, and remembering the quasi-constant relationship between refractivity and density, it seemed pertinent to consider function-t equations of other types that have been found suitable for representing the observed density of water. Only one such type of formula has been used for the range 0 to 40° C for water.[3] It was published by Thiesen, Scheel, and Diesselhorst,[4] who represented their data obtained at the Reichsanstalt in 1896, with a four-constant equation of the form

$$(1-d)=\frac{(t-A)^2}{B}\cdot\frac{t+C}{t+D}, \tag{1}$$

where A is the temperature of maximum density, and the unit of density is 1 g per milliliter. Moreover, Thiesen[5] later found this same form of equation to be approximately adequate over the larger temperature range 0 to 100° C. He also obtained somewhat better results by extending the equation to six parameters, of which two were arbitrarily selected. The final comparison between his formulas is conditioned, however, by the fact that in both cases his computations for determining the constants were limited to five significant figures.

Preliminary computations made by the authors indicated that an equation of the same type and limited to the four-constant form

$$n_t=n_{\max}-\frac{(t-A)^2}{B}\cdot\frac{t+C}{t+D} \tag{2}$$

would be useful for representing refractive index, but a transformation was desirable because in this case no assumption concerning an exact value for the maximum index of water was advisable. Consequently, since index data at 20° C were more numerous and somewhat more reliably determined than those for other temperatures, eq 2 was written for a temperature of $[20+(t-20)]°$ and for $n_{\max}$ its value in terms of n_{20} was substituted. The result is

$$n_t=n_{20}+\frac{C'(A')^2}{BD'}-\frac{[(t-20)+A']^2}{B}\cdot\frac{(t-20)+C'}{(t-20)+D'}, \tag{3}$$

where $A'=20-A$, $C'=20+C$, and $D'=20+D$. Then after combining terms, eq. 3 may be written in simpler form as

$$n_t-n_{20}=-\frac{\overline{B}(t-20^3)+\overline{A}(t-20)^2+\overline{C}(t-20)}{(t+\overline{D})\times 10^7}, \tag{4}$$

where the new parameters in terms of those in eq 2, are

$$\left.\begin{aligned}\overline{B}&=\frac{1}{B}\times 10^7\\ \overline{A}&=\frac{(C-2A+60)}{B}\times 10^7\\ \overline{C}&=\frac{20-A}{B}\left[40+C-A+\frac{(A+D)(20+C)}{20+D}\right]\times 10^7\\ \text{and}\quad \overline{D}&=D.\end{aligned}\right\} \tag{5}$$

[3] Chappuis, for his seventh-decimal-place densities of water determined in 1891 and 1897 at the International Bureau, at Paris, (Travaux et Mémoires du Bureau International des Poids et Mesures **13**, D19 (1907)) used three separate equations, cubics in t, to cover the temperature range 0 to 41° C.

[4] Wiss. Abhandl. physik-tech. Reichsanstalt **3**, 67 (1900).

[5] Wiss. Abhandl. physik-tech. Reichsanstalt **4**, 30 (1904).

For curve fitting, eq. 4 is more convenient than eq 2 from which it was obtained. Approximate values of the parameters are readily found by using eq 4 in the form

$$10^7(n_{20}-n_t)=\frac{(t-20)^3}{t}\overline{B}+\frac{(t-20)^2}{t}\overline{A}+\frac{(t-20)}{t}\overline{C}+\frac{n_t-n_{20}}{t}\overline{D}, \quad (6)$$

and for betterments by least squares, one writes

$$10^7\Delta(n_{20}-n_t)=\frac{(t-20)^3}{t+\overline{D}}\Delta\overline{B}+\frac{(t-20)^2}{t+\overline{D}}\Delta\overline{A}+\frac{t-20}{t+\overline{D}}\Delta\overline{C}+\frac{n_t-n_{20}}{t+\overline{D}}\Delta\overline{D}, \quad (7)$$

provided it can be assumed that errors in temperature are small in their effect on index as compared with those errors otherwise involved in the index measurements.

For representing the index of water it is desired to compare the suitability of eq 4 with that of a power series employing the same (four) or a slightly greater number of parameters. A power series

$$n_t=n_0-10^{-7}[at+bt^2+ct^3+dt^4+\cdots], \quad (8)$$

as usually written for expressing refractive index, is easily transformed to

$$n_t-n_{20}=-10^{-7}[(t-20)a+(t^2-\overline{20}^2)b+(t^3-\overline{20}^3)c+(t^4-\overline{20}^4)d+\cdots] \quad (9)$$

after substituting for n_0 its value in terms of n_{20}. Equation 9, being linear in the parameters, is much more convenient for curve fitting than is eq 4 with which it is to be compared.

II. TESTS WITH REFRACTIVE-INDEX DATA

In previously testing [6] the validity of dispersion equations which were to be used in the adjustment and representation of precise data on the refractivity of distilled water, the available preliminary data on dispersion were more numerous and more suitably distributed throughout the spectrum than were the definitive data. Consequently their use for the tests was in these respects preferable to the use of the definitive data themselves. In the present instance a few preliminary measurements of index had been made at only 10 temperatures, not evenly spaced, between 10 and 60° C, whereas, in the definitive program with approved procedures, many observations were made at 13 temperatures in 5° steps from 0 to 60° C, inclusive. Consequently, it seemed preferable to use the definitive data in testing the function-t equations.

1. ADJUSTMENT OF OBSERVATIONS

All details concerning these observations are to be given in a subsequent paper. Here it is sufficient to state that they consist of (averaged) data at each of 133 temperature–wave-length coordinates within the ranges 0 to 60° C and 4047 to 7065 A. By the method of least squares these indices at each of the temperatures were carefully represented by dispersion equations of the form

$$n_t^2=a_t^2-k_t\lambda^2+\frac{m_t}{\lambda^2-l_t^2}, \quad (10)$$

[6] J. Research NBS 17, 639-650 (1936) RP934.

which had previously been tested and found particularly suitable for this purpose. These equations constitute what may be termed an isothermally adjusted system based on the actual observations. They were used for computing 13 sodium-lines indices of refraction of water which in turn were considered as "observed" values for purposes of testing function-t equations. For each temperature the corresponding dispersion equation permits the computation of indices which are to some extent free from accidental errors of observation. Having in mind the favorable results of previous tests of this dispersion equation, and considering particularly its use here for wave lengths near the midrange, it seems likely that this elimination of accidental error is a more important matter than the possible introduction of systematic errors of a functional nature.

2. ADJUSTED VALUES OF FUNCTION-t CONSTANTS

There being only 13 observed values of n_t, only 12 values of $n_t - n_{20}$ were available for use in adjusting the parameters of proposed function-t equations, and it was imperative to select an equation that could be satisfactorily used with a minimum number of such parameters. Accordingly, eq 6 and 7 were used in turn in determining the parameters of eq 4 as written for four parameters only, and the formula

$$(n_t - n_{20})_D = -\frac{6.2609(t-20)^3 + 2373.16(t-20)^2 + 77170.3(t-20)}{(t+66.9388)\times 10^7} \tag{11}$$

was thus obtained.

Similarly, for eq 9, first four and then six parameters were used, and adjustments were made by least squares. These computations yielded the formulas

$$(n_t - n_{20})_D = -10^{-7}[9.868(t-20) + 27.3555(t^2 - \overline{20}^2) - 0.206310(t^3 - \overline{20}^3) + 0.00096718(t^4 - \overline{20}^4)], \tag{12}$$

and

$$(n_t - n_{20})_D = -10^{-7}[1.158(t-20) + 27.6358(t^2 - \overline{20}^2) - 0.166690(t^3 - \overline{20}^3) - 0.00168363(t^4 - \overline{20}^4) + 0.0000554067(t^5 - \overline{20}^5) - 0.000000381815(t^6 - \overline{20}^6)], \tag{13}$$

respectively.

3. RELATIVE GOODNESS OF FIT AND CHI-TEST

The results of tests and intercomparisons of formulas 11, 12, and 13 are given in table 1, where many of the entries are self-explanatory, and all are made by steps strictly comparable with those discussed in connection with table 1 of a previous paper on the validity of dispersion formulas.[7] It appears that the four-constant power series, formula 12, is decidedly inferior to the others and that the six-constant power series, formula 13, is better than the four-constant formula 11. The probable error of the so-called observations is not over $\pm 0.45\times 10^{-6}$ to judge from the tabulated values, while from the data themselves an estimate of ± 0.55 was made. Consequently, $\pm 0.50\times 10^{-6}$ was adopted as the a priori estimate of probable error for use in computing

[7] J. Research NBS 17, 639–650 (1936) RP934.

other probabilities. As a result it seems that the four-constant formula 11, even if completely suitable in form, would by chance alone in 3 of 100 such tests appear less perfect than is here found. This does not seem to be a high recommendation, but it should be remembered that this computation of probability depends in an important degree on the a priori estimate of the probable error. Also since only one test of this formula has been made it can by chance alone be one having an unfavorable result. In any event the pertinent requirement is mere serviceability within limits of error, and not perfection. Figure 1, a graphic comparison of these formulas by means of the individual residuals, enables one to see that any imperfection existing in the four-constant formula 11 cannot be serious in sixth-decimal refractometry.

TABLE 1.—*Statistical comparison of function-t formulas for* $\Delta n = n_t - n_{20}$

	(Thiesen type)	(Power series)	(Power series)
Designation of formula	11	12	13
Number of independent parameters	4	4	6
Number of plus residuals (observed minus computed Δn)	7	7	5
Number of minus residuals	5	5	7
Number of changes in sign of adjacent residuals	6	5	8
Number of nonchanges in sign of adjacent residuals	5	6	3
$10^2\Sigma r \equiv$ algebraic sum of residuals	−0.33	+6.15	+0.11
$10^6\times$ algebraic average residual	−.03	+0.51	+.01
$10^2\Sigma\lvert r\rvert \equiv$ arithmetic sum of residuals	8.16	19.93	4.56
$10^6\times$ arithmetic average residual	0.68	1.66	0.38
$10^6\times$ median residual	.5	1.9	.4
$10^{11}\times\Sigma r^2$	9.51	49.75	2.66
$10^6\times$ estimated P.E. (assuming that existing degree of fit can be worse by chance alone in 50% of such tests)	±0.73	±1.68	±0.45
$10^6\times$ estimated P.E. of estimated P.E.	±.12	±0.28	±.09
Number of observations minus number of parameters	8	8	6
$\chi^2=\Sigma r^2/(1.483\ \text{P.E.})^2$, where P.E. is estimated a priori as $\pm 0.50\times 10^{-6}$	17.3	90	4.8
Probability of worse fit by chance alone if P.E. is estimated a priori as 0.50×10^{-6} in index	0.03	Very small	0.54
Odds that formula is imperfect in form	33 to 1	Very great	1 to 1

III. TESTS WITH DENSITY DATA

The distribution of "observed" values in figure 1 suggests, however, that formula 11 leads to values that are slightly too high near 30 and near 55° C. Although these discrepancies are not large, as compared with possible experimental errors, they are of interest as possible peculiarities, either in formula 11 or in the behavior of water, near these temperatures. The fact that formula 13, with six independently adjusted constants, more nearly accords with the 12 observed values is in large measure forced by the large ratio of number of parameters to number of observed values. More refractivity data for use in testing formula 11 would be desirable, but unfortunately they are not at present available.

In the absence of such additional refractivity data, it seemed appropriate to examine systematically the Chappuis [8] data on density of water to seven decimal places as determined in 1891 and 1897 at the International Bureau, at Paris. The fitting of a four-parameter equation of the Thiesen type to this data might reveal discrepancies

[8] See footnote 3, p. 206.

in density similar to those in index that have been discussed in the preceding paragraph. Under such circumstances one would seriously consider the advisability of employing more parameters in precisely representing thermal variations in refractive index, even at the cost of obtaining more index data for their proper evaluation.

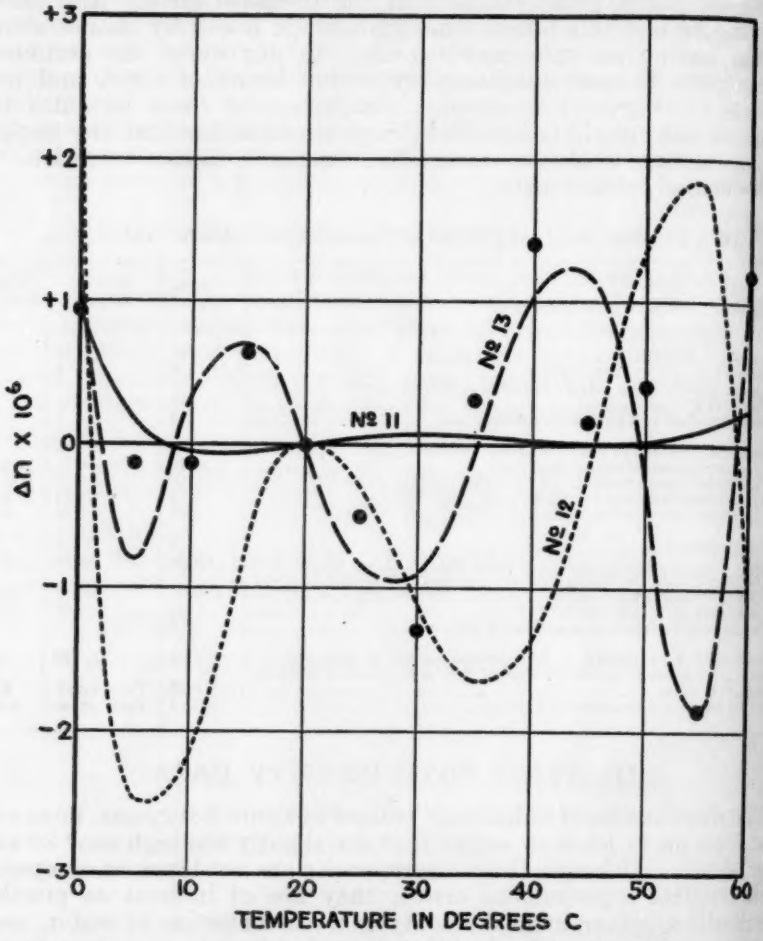

FIGURE 1.—*Comparison of function-t formulas for thermal variation in the refractive index, n_D, of water.*

Formulas 11, 12, and 13, with 4, 4, and 6 parameters, respectively, were adjusted by least squares to fit the sodium-lines indices of distilled water as computed by dispersion equations representing data for various wave lengths taken independently at each of 13 temperatures. Circular dots represent residuals for such sodium-lines indices, and lines represent residuals for indices computed as functions of t. The reference line $\Delta n=0$ corresponds to indices computed by a general interpolation formula (based, like formula 11, on eq 4 and 10) to fit all approved data taken for several wave lengths.

For a systematic examination of this sort, Chappuis' data are superior to those of Thiesen, Scheel, and Diesselhorst in that they are well distributed throughout the range 0 to 41° C, whereas the others consist of close groups spaced at approximately 5° intervals. This examination of density data seemed especially desirable because, as indicated by Chappuis' tabulated comparison, the two similar tables

of density based, respectively, on these two sets of data diverge in such manner that the difference between them shows a very noticeable succession of maxima and minima and is increasing very rapidly at 41° C. Since Chappuis had used three separate density equations, cubics in t, to cover this temperature interval, it seemed that this systematic divergence might be an indication of the limitations of the much simpler Thiesen equation.

1. REEXAMINATION OF THE CHAPPUIS OBSERVATIONS

To make this test effectively, but with a minimum of labor, a value for A of eq 1 was directly determined after differentiation of the first Chappuis equation, namely, one for the temperature interval 0 to 10.3° C. Then densities at 2.5° intervals were taken from the Chappuis table, 17 observational equations were formed, and values for B, C, and D were computed by least squares (assuming the temperatures as exact). The resulting formula

$$(1-d)=\frac{(t-3.9863)^2}{508929.2}\cdot\frac{t+288.9414}{t+68.12963} \tag{14}$$

was used in computing densities for comparison with each of the 114 values determined experimentally by Chappuis.

The sum of the squared residuals is reduced to 71 per cent of the corresponding sum obtained when the observations are subtracted from the entries in the Chappuis table. This published table was, however, a result of implicit weightings of the observed values and it seemed desirable to make a comparison which would include those weights. It appears that 30 observations of the first set in 1891 were given equal weight with 45 of the second set and then 39 determinations in 1897 affected the tabulated values as much as all of the 1891 data. Consequently, the effective weights were proportional to the numbers 0.650, 0.433, and 1.00, respectively, for the three sets in chronological order. Using these weights, the sum of the weighted squared residuals is, for formula 14, 68 percent of the corresponding sum for the Chappuis table computed by its three separate formulas, each with three powers of t. In other words, then, the weightings seem to have little or no effect on the comparative merits of the two sets of computed values.

The (unsquared) residuals for formula 14, have been carefully examined for evidence of systematic trends. In figure 2 the weighted residuals and also the corresponding residuals for the Chappuis table are plotted for comparison. The systematic deviation between the data and the Chappuis table (computed by the triad of cubics in t) is particularly noticeable for temperatures near 15° C. Of 16 observed values between 11 and 20° C all are higher than the tabulated densities and the average of these residuals is $+14 \times 10^{-7}$. On the other hand, there seems to be no systematic deviation between the observations and the values defined by formula 14.

2. RESULTS OF READJUSTMENT

Since the Thiesen, Scheel, and Diesselhorst table agrees with their (independently adjusted) observed values within the limits $+7$ and -4×10^{-7}, it may be concluded from figure 2 that the maximum discrepancies between observations at the International Bureau and at the

PTR are appreciably smaller than has hitherto appeared, especially at temperatures near 25 and 40° C.

Formula 14 has been used for computing table 2 in which are listed the revised values of density which, according to this analysis of the Chappuis data, should be substituted for the table now extant, if more than five digits are to be used. Many changes in listing are larger than $\pm 20 \times 10^{-7}$, and at 12 to 15° C the change is approximately ¼ per cent of $(1-d)$. The maximum excess of this new table over that given by Thiesen, Scheel, and Diesselhorst is only $+62 \times 10^{-7}$ at

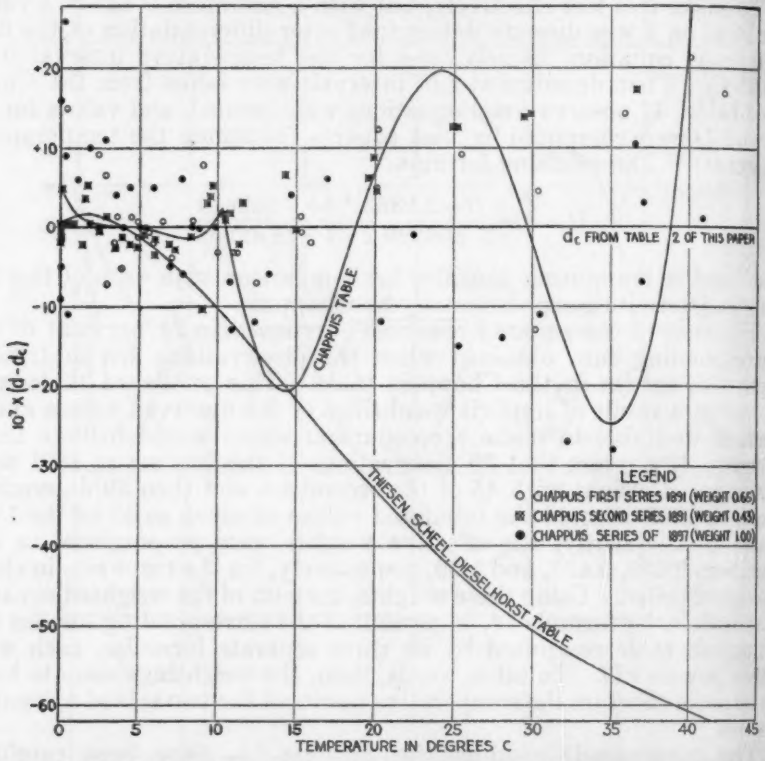

FIGURE 2.—*Weighted residuals for density of distilled water as compared with computed density, d_c, from table 2 of this paper.*

Note that all of Chappuis' observed values are higher than his tabular values from 11 to 20° C, while from 20.5 to 29.5° C all his observations appear lower. (For unweighted residuals at the 23 observed points within these temperature intervals, there are two exceptions to this statement.)

41° C, as compared with the old difference of $+111 \times 10^{-7}$. Comparison of certain mean coefficients of expansion taken from this revised table 2 and from Chappuis' table, shows differences of several tenths of 1 percent.

At this time it is not desirable to compute a corresponding table of refractive index by use of formula 11, because some readjustment of the constants will probably result when all approved data are more freely adjusted by use of a combined function-t and dispersion formula for indices over the whole temperature–wave-length surface.

TABLE 2.—*Density of distilled water computed from Chappuis' observations by the formula* $(1-d)=\frac{(t-3.9863)^2}{508929.2}\cdot\frac{t+288.9414}{t+68.12963}$

Temperature, °C		Tenths of degrees									
		0	1	2	3	4	5	6	7	8	9
0	0.999	8676	8743	8808	8871	8933	8993	9051	9107	9161	9214
1		9265	9314	9362	9407	9451	9493	9534	9573	9610	9645
2		9678	9710	9740	9769	9796	9821	9844	9866	9886	9905
3		9922	9937	9950	9962	9972	9981	9988	9993	9997	9999
4	1.000	0000	·9999	·9996	·9992	·9986	·9979	·9970	·9960	·9948	·9934
5	0.999	9919	9902	9884	9864	9843	9820	9796	9770	9742	9713
6		9683	9651	9618	9583	9546	9508	9469	9428	9386	9342
7		9297	9250	9202	9153	9102	9049	8995	8940	8883	8825
8		8765	8704	8642	8578	8513	8446	8378	8309	8238	8166
9		8092	8017	7941	7863	7784	7704	7622	7539	7454	7368
10		7281	7193	7103	7012	6919	6825	6730	6634	6536	6437
11		6336	6234	6131	6027	5922	5815	5706	5597	5486	5374
12		5261	5146	5030	4913	4795	4675	4554	4432	4309	4184
13		4059	3932	3803	3674	3543	3411	3278	3143	3007	2870
14		2732	2593	2453	2311	2168	2024	1879	1732	1584	1436
15		1286	1134	0982	0828	0674	0518	0360	0202	0043	·9882
16	.998	9721	9558	9394	9229	9062	8895	8726	8557	8386	8214
17		8041	7867	7691	7515	7337	7158	6979	6798	6616	6433
18		6248	6063	5877	5689	5501	5311	5120	4928	4735	4541
19		4346	4150	3953	3754	3555	3355	3153	2950	2747	2542
20		2336	2130	1922	1713	1503	1292	1080	0867	0653	0438
21		0221	0004	·9786	·9567	·9346	·9125	·8903	·8679	·8455	·8230
22	.997	8003	7776	7547	7318	7088	6856	6624	6390	6156	5921
23		5684	5447	5208	4969	4729	4487	4245	4002	3758	3512
24		3266	3019	2771	2522	2272	2021	1769	1516	1262	1007
25		0751	0494	0237	·9978	·9718	·9458	·9196	·8934	·8671	·8406
26	.996	8141	7875	7608	7340	7071	6801	6530	6258	5986	5712
27		5437	5162	4886	4608	4330	4051	3771	3490	3208	2926
28		2642	2358	2072	1786	1499	1211	0922	0632	0341	0049
29	.995	9757	9463	9169	8874	8578	8281	7983	7684	7384	7084
30		6783	6480	6177	5874	5569	5263	4956	4649	4341	4032
31		3722	3411	3099	2787	2473	2159	1844	1528	1211	0894
32		0575	0256	·9936	·9615	·9293	·8970	·8647	·8322	·7997	·7671
33	.994	7344	7016	6688	6359	6028	5698	5366	5033	4700	4365
34		4030	3694	3358	3020	2682	2343	2003	1662	1320	0978
35		0635	0291	·9946	·9600	·9254	·8907	·8559	·8210	·7860	·7510
36	.993	7159	6807	6454	6100	5746	5391	5035	4678	4321	3962
37		3604	3244	2883	2522	2160	1797	1433	1068	0703	0337
38	.992	9970	9603	9234	8865	8495	8125	7753	7381	7008	6634
39		6260	5884	5508	5132	4754	4376	3997	3617	3236	2855
40		2473	2090	1707	1323	0938	0552	0165	·9778	·9390	·9001
41	.991	8612	8221	7830	7439	7046	6653	6259	5864	5469	5073
42		4676									

IV. CONCLUDING DISCUSSION

Whereas precise tests in representing thermal variations in the refractive index of water indicated the adequacy of a four-constant formula of the Thiesen type, some question remained because the data were grouped at relatively few temperatures from 0 to 60° C and, moreover, because an implicit challenge existed in that Chappuis had used a triad of cubics in t to cover the smaller temperature interval 0 to 41° C in the related field of density of water. Examination of Chappuis' data has revealed, however, that they may be even more satisfactorily represented by an equation of the Thiesen type than by the cubics. The density residuals show no systematic departure from this four-constant formula even near 30° C, where a small departure in refractive index was suggested by figure 1.

Insofar as conditions at 30° are concerned, this negative result may occur merely because the precision of either index or density measurements is not sufficiently high; or it is, of course, possible that the phenomena of absorption are sufficiently important to influence index in such manner that, considered as a function of temperature, index is not exactly comparable with density at or beyond the limits of precision reached in these investigations. However this may be, for all practical purposes formula 11, of the Thiesen type, satisfactorily represents the refractivity of distilled water as a function of temperature. It is much superior to a power series having the same number of constants.

Aside from the ease with which they may be handled, the use of power series in representing either the refractivity or the density of water should probably be considered as a practical expedient acceptable only as an approximately satisfactory solution of a difficult problem. If, however, it is desired to secure validity of representation within a very few parts per million and to use only a minimum number of parameters, then the tests herein reported seem highly favorable to the use of that type of equation which Thiesen used for density.

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COMPRESSIVE STRENGTH OF STRUCTURAL TILE MASONRY

By Douglas E. Parsons and David Watstein

ABSTRACT

In cooperation with the Housing Division of the Federal Emergency Administration of Public Works, 6 walls and 30 wallettes were tested. The object was to determine how differences in tile design or kind of mortar affected the compressive strength of masonry walls in a combination of brick-facing and end-construction tile under eccentric loads. The walls were of structural clay tile with a facing of brick, alike in all respects except design of the tile. Different mortars as well as tiles of different designs were used in constructing the wallettes. All masonry specimens were tested at the age of 2 months.

As the loads were applied on the walls during the compressive tests, the rate of deformation increased with increasing loads, because of the yielding of the mortar. The mortar, composed of a mixture of one part cement, one part lime, and six parts of sand, by volume, crushed in the bed joints for the tile. The strengths of the walls were roughly proportional to the thickness of the face shells of the tiles. The crushing of the mortar in the bed joints also was the first sign of impending failure of the wallettes, except for those built with mortars rich in portland cement.

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I. INTRODUCTION

At the request of the Housing Division, Federal Emergency Administration of Public Works, the National Bureau of Standards tested 6 walls and 30 wallettes to determine the effects of differences in either the design of the tile or the kind of mortar on the compressive strength of tile masonry. The six walls were of structural clay tile with facings of brick; they were similar in all respects except the design of the tiles, there being two walls each of three different kinds of tile. The wallettes included three each of seven kinds of tile and one mortar, and three each of four kinds of mortar with the same type of tile.

II. MATERIALS

1. TILES

The designs of the tiles are illustrated in figures 1 and 2; figure 1 shows end views of stretcher tiles, and figure 2 illustrates both stretcher and bonding tiles. All of the tiles were made from fire clay. Powdered coal was mixed with the clay used in forming the lightweight tiles *E* and *F*, resulting in a material of lighter weight than that of the other tile, because of the burning out of the coal during kiln firing.

Ten each of tiles *A*, *B*, and *C*, and five each of the others were tested according to the Tentative Methods of Sampling and Testing Structural Clay Tile (C 112–35T) of the American Society for Testing Materials,[1] insofar as these methods applied. The results of the tests are given in table 1.

TABLE 1.—*Physical properties of the structural clay tiles*

Each value in the table is the average from tests of 10 tiles each of types *A*, *B*, and *C*, and of 5 tiles each of types *D*, *E*, *F*, and *G*.

Type[1]	Dimensions			Thickness of face shells	Weight			Compressive strength (cells vertical)		Absorption	
	Thickness	Width	Length		Gross volume	Net volume	Per unit of face area	Gross area	Net area	24-hr submersion	1-hr boiling
	in.	in.	in.	in.	lb/ft³	lb/ft³	lb/ft³	lb/in.²	lb/in.²	%	%
A	7.90	11.90	7.50	0.75	51.0	143	33.42	3,750	10,600	2.91	3.57
B	7.95	12.00	7.50	1.50	79.8	141	52.77	5,300	9,400	3.66	4.17
C	7.95	12.05	7.60	1.13	59.1	137	39.11	4,350	10,050	3.88	5.38
D	7.90	11.90	7.50	1.37	69.2	140	45.32	4,000	7,950	4.68	5.73
E[2]	7.85	11.80	7.50	1.50	53.5	95	35.24	2,400	4,300	10.44	25.29
F[2]	7.80	11.95	7.50	1.40	45.1	92	29.40	2,000	4,050	15.84	27.56
G	7.90	12.00	7.60	1.50	60.3	137	39.68	4,600	10,400	5.40	6.98

[1] Design of the tiles are illustrated in figures 1 and 2.
[2] Light-weight (highly porous) tile.

2. BRICKS

The bricks were of surface clay, formed by the stiff-mud side-cut process. Ten of the bricks, selected at random, were measured and tested according to the Tentative Methods of Testing Brick (C 67–35T) of the American Society for Testing Materials.[2]

[1] Proc. Am. Soc. Testing Materials **35**, I, 807 (1935).
[2] Proc. Am. Soc. Testing Materials **35**, I, 791 (1935).

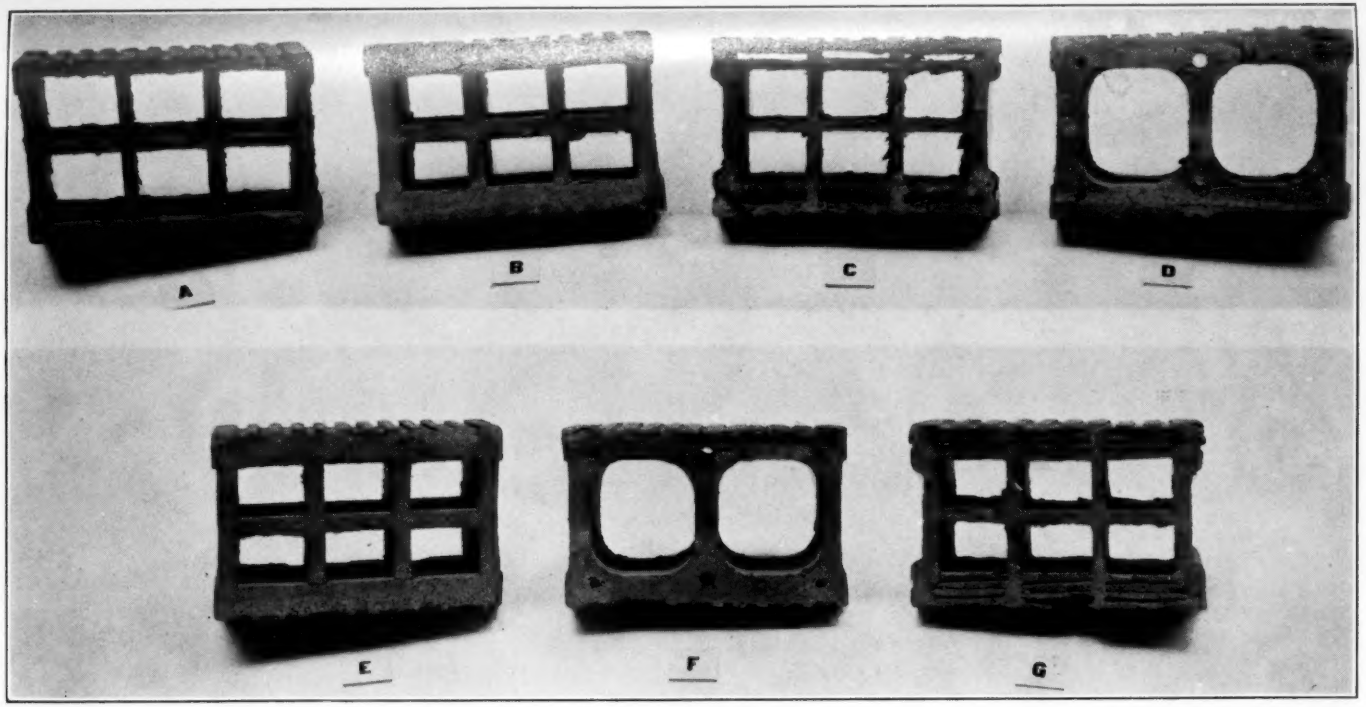


FIGURE 1.—*Structural clay tiles.*

Tiles *A* were used in walls *A-1* and *A-2*; *B* in walls *B-1* and *B-2*; and *C* in walls *C-1* and *C-2*. Tiles of each type were used in the wallettes according to the schedule given in table 3.

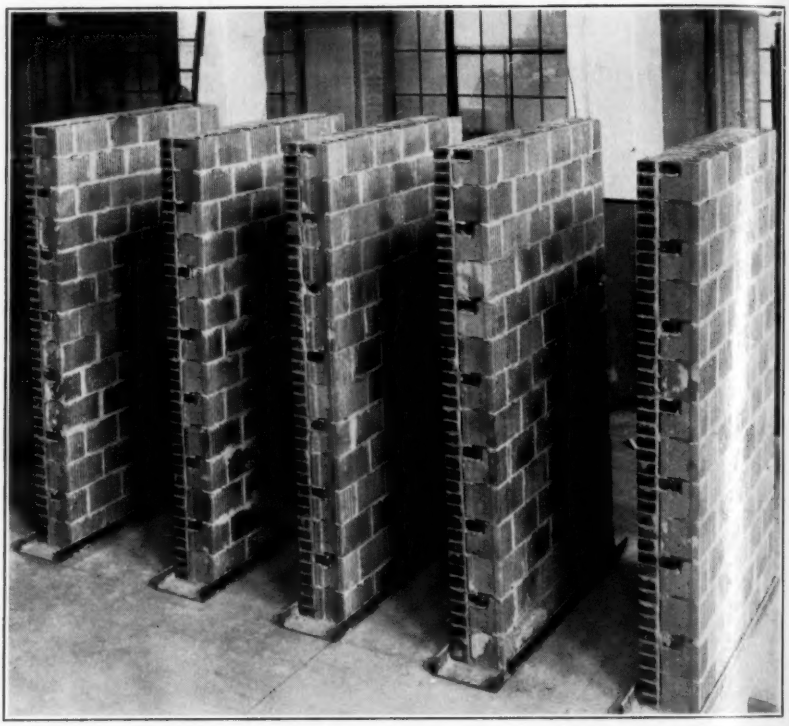
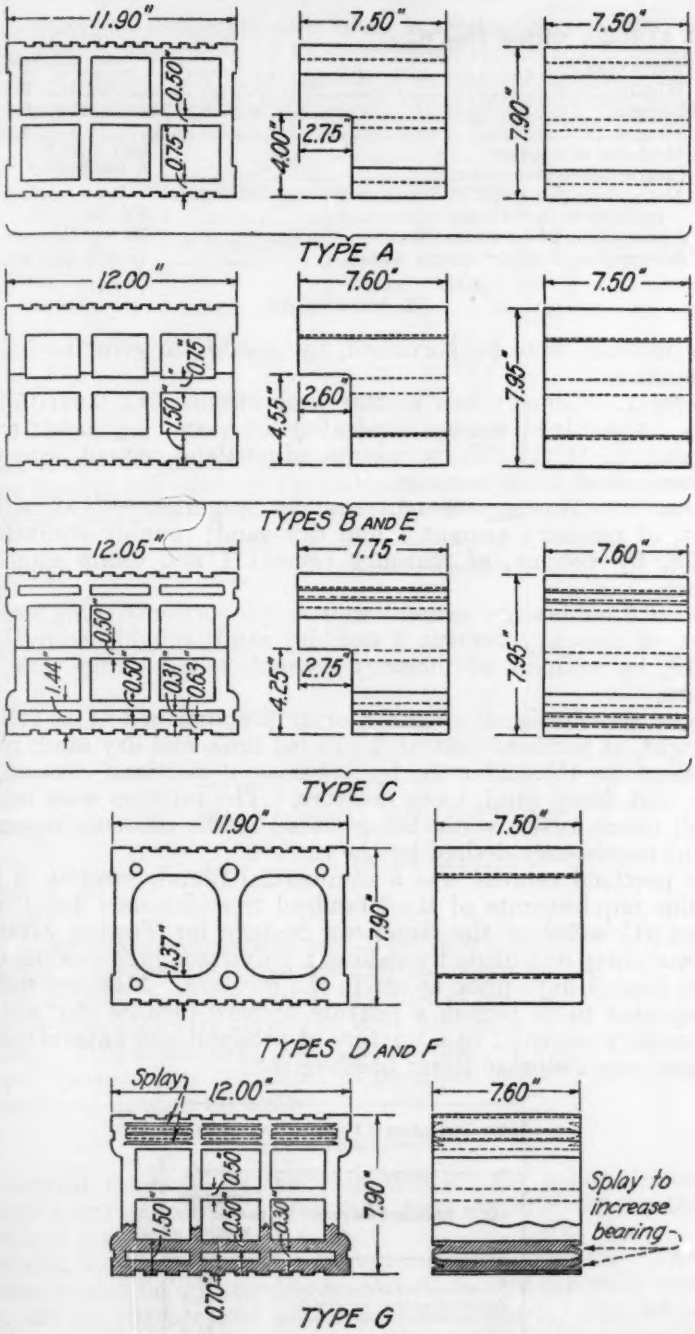


FIGURE 4.—*View of five of the walls in the laboratory.*



* No bonding tile were used with types D, E, F and G.

FIGURE 2.—*Designs of tiles used in walls and wallettes.*

Tiles *A* were used in walls *A-1* and *A-2*; *B* in walls *B-1* and *B-2*; and *C* in walls *C-1* and *C-2*. Tiles of each type were used in the wallettes according to the schedule given in table 3. No bonding tile were used with types *D*, *E*, *F*, and *G*. Dimensions shown for tiles *E* and *F* are approximate; average values for each type of tile are given in table 1.

The average values follow:

Thickness	2.26 in.
Width	3.78 in.
Length	8.14 in.
Weight	4.95 lb.
Modulus of rupture	805 lb/in.^{2}
Compressive strength	5,400 lb/in.^{2}
Absorption per brick in 3 min with one flat face in contact with water	3.4 oz.
Absorption, 24-hr submersion	10.5% (by weight).
Absorption, 5 hr in boiling water	13.3% (by weight).

3. MORTARS

The mortars were proportioned, by weight, to give the following compositions:

Mortar 1.—Cement-lime mortar proportioned 1C: 0.42L:5.1S, by weight, of portland cement, hydrated lime, and dry sand; roughly equivalent to 1C:1L:6S, by volume, of portland cement, lime putty, and damp sand, loose measure.

Mortar 2.—Masonry cement mortar proportioned $1M_1$:4.0S, by weight, of masonry cement 1 and dry sand; roughly equivalent to $1M_1$:3S, by volume, of masonry cement 1 and damp sand, loose measure.

Mortar 3.—Masonry cement mortar proportioned $1M_2$:3.43S, by weight, of masonry cement 2 and dry sand; roughly equivalent to $1M_2$:3S, by volume, of masonry cement 2 and damp sand, loose measure.

Mortar 4.—Portland cement mortar proportioned 1C:0.11L:2.6S, by weight, of portland cement, hydrated lime, and dry sand; roughly equivalent to 1C:0.25L:3S, by volume, of portland cement, lime putty, and damp sand, loose measure. The mortars were mixed in a small batch mixer, water being added in the amounts required to give the consistency desired by the mason.

The portland cement was a commercial brand, samples of which met the requirements of the Standard Specifications for Portland Cement (C 9–30) of the American Society for Testing Materials.[3] The lime putty was made by slaking a pulverized high-calcium quicklime at least 3 days prior to use in the mortars. Masonry cement 1 was reported to be largely a mixture of blast-furnace slag and lime, and masonry cement 2 as a mixture of portland and natural cements. The sand was Potomac River building sand.

Size distribution of Potomac River building sand

U. S. Standard Sieve no.	Percentage passing (by weight)
4	100.0
8	99.4
16	94.4
30	75.2
50	14.0
100	1.0
200	0.5

[3] 1930 Book of ASTM Standards, II, 3.

The cementing materials used in each of the mortars were tested according to the methods of Federal Specification for Masonry Cement (SS–C–181). All met the requirements of this specification. The compressive strengths of the 2-inch cubes of mortar, 1:3, by weight of cementing material to sand and having a flow of 105 ±5 percent, were as follows:

With cement for mortar	Compressive strength at—	
	7 days	28 days
	lb/in.²	lb/in.²
1	790	1,120
2	400	660
3	410	810
4	1,670	2,300

The average compressive strengths of 2-inch cubes molded from the mortars used in the walls and wallettes and aged in the damp-storage room of the concrete laboratory until tested were as follows:

Mortar	Compressive strength at—	
	7 days	28 days
	lb/in.²	lb/in.²
1	360	1,040
2	340	1,110
3	360	670
4	2,540	3,870

III. WALLS AND WALLETTES

1. DESCRIPTION OF WALLS

(a) TYPES

The walls were a combination of brick facing and tile backing with a masonry bond, as illustrated in figure 3. Figure 4 shows five of the walls, and figure 5 shows typical sections of the walls and wallettes. The walls were approximately 9 ft, 3 in. high; 5 ft, 1 in. long; and 12.3 in. thick. Two walls each were constructed of tiles *A*, *B*, and *C*. Mortar 1 (proportions 1:0.42:5.1 of portland cement, hydrated lime, and sand) was used in all walls.

(b) WORKMANSHIP

A contract for building the walls was let, for a lump sum, to a masonry contractor whose workmen were experienced in the construction of masonry walls.

The walls were constructed on structural-steel channels. The channels were leveled before starting construction, and the walls were kept plumb and the courses level as the work progressed. The bricks were wetted before laying; the tiles were dry. The mortar for the bed joints in the brickwork was spread to uniform thickness (not furrowed). Mortar was applied to the ends of stretcher bricks and to the edges of header bricks before laying; after laying, the filling of the cross joint was completed (if necessary) by "slushing." The facing between two

consecutive header courses was constructed, and the back surface coated with a mortar parging about ⅜ in. thick before setting the tile of the backing. Except for the bed of the header brick, the mortar in the tile backing was applied only along the face shells, as illustrated in figures 3 and 5.

(c) AGING

The walls were built during the period from November 27 to December 4, 1935, and remained in the laboratory until tested at ages ranging from 57 to 62 days.

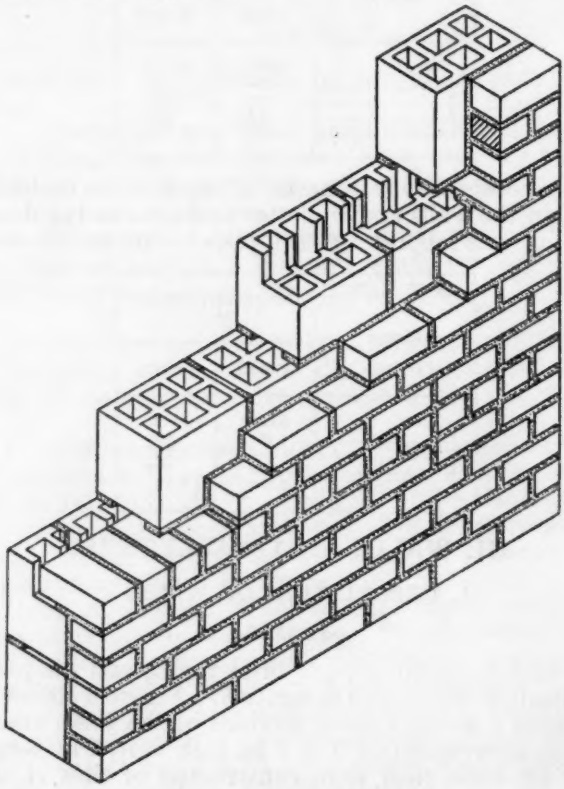


FIGURE 3.—*Details of the walls.*

Joints in the brick facing were filled with mortar and the back of the stretcher bricks of the facing was parged with mortar. The mortar was spread only along the two face shells of the tiles.

2. DESCRIPTION OF WALLETTES

(a) TYPES

Each wallette consisted of three tiles set on end with their faces and cells in alignment, as illustrated in figure 5. The wallettes were approximately 2 ft high, 1 ft long, and 7.9 in. thick. Only two shells on opposite faces of each tile were bedded in mortar. Using mortar 1, three wallettes each were constructed of tiles *A*, *B*, *C*, *D*, *E*, *F*, and *G*. In addition, there were three wallettes each of tile *B* made with each of mortars 2, 3, and 4.

(b) AGING

The wallettes were constructed in the laboratory and were kept until tested (2 months) in a room in which the temperature of the air was maintained at 70 ± 2° F. The tiles were dry when set. The wallettes were built during the month of January 1936. The extraordi-

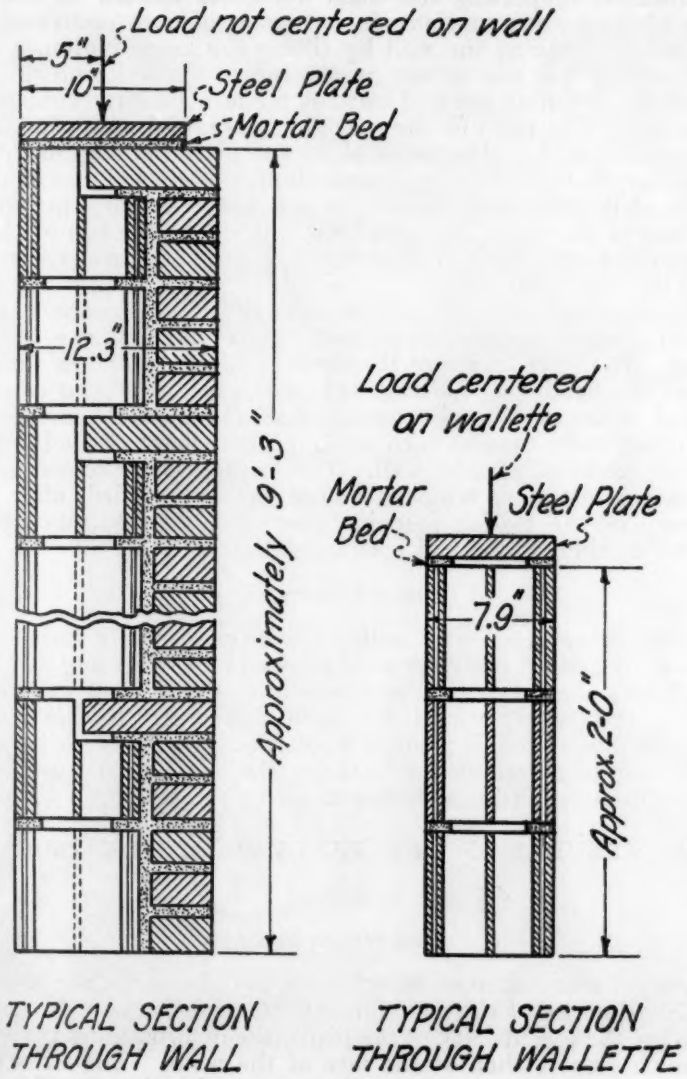


FIGURE 5.—*Typical sections of walls and wallettes.*

narily cold weather and the attendant low relative humidity in the storage room during the aging, together with the free circulation of air around the specimens, probably produced an abnormally rapid drying of the mortar in the wallettes. The highly unfavorable curing conditions would be expected to result in strengths lower than normal, especially for mortars 2, 3, and 4, as these were of compositions which would tend to dry more rapidly than mortar 1.

3. METHODS OF TESTING

(a) WALLS

The walls were tested in compression under eccentric loading in the 10,000,000-lb capacity machine at the National Bureau of Standards. The channels supporting the walls were first bedded on the lower platen of the testing machine in a mortar of neat plaster of paris. Then, after plumbing the wall by tilting the lower platen, a cap of the plaster mortar was spread on the top of the wall and the upper head of the machine lowered until it made a uniform contact with the mortar. The head of the machine was raised after the capping had hardened and a plane steel plate was placed on top of the wall. A steel bar, $\frac{5}{16}$ in. square in cross section, was then set on the plate, the axis of the bar being parallel to and a distance of 5 in. from the back face of the wall. The load was applied to the top of the wall through this bar, resulting in a compressive load having an eccentricity of 1.15 in.

Vertical compressometers were attached near each corner of the wall and horizontal extensometers on each face at midheight, as shown in figure 6. The gage length of the vertical compressometers (about 95 in.) was the height of the wall, minus the height of two courses of tile; that of the horizontal extensometers was about 45 in. The dial micrometers were read at each 50-lb/in.^{2} increment of load based on the gross sectional area of wall. The loading was stopped and the compressometers were removed before the walls failed, after which the pump of the testing machine was operated continuously until after the maximum load had been passed.

(b) WALLETTES

The bearing surfaces of the wallettes were capped with a neat mortar of plaster of paris. The caps were allowed to harden and dry before the wallettes were tested. For the compressive tests a wallette was placed on the lower platen of a 300,000-lb capacity testing machine, and the load was applied through a spherical bearing block in contact with the top of the specimen. During the loading the machine was run continuously until the maximum load was passed.

IV. RESULTS OF THE TESTS WITH DISCUSSION

1. WALLS

(a) STRESS-STRAIN DIAGRAMS

Average stress-deformation relations for the walls are shown in figure 7. Because of the combined effects of differences in construction and of the eccentricity of the loads, the deformations at the back were much greater than at the face of the walls. The stress-strain diagrams for the back are decidedly curved with the rate of increase of strain becoming larger as the stress increased, even for loads below one-half of the maximum load for the walls. In this respect these curves show relations similar to those found in other tests of masonry built with lime mortar or comparatively weak cement-lime mortars.[4]

[4] See, for example: BS Tech. Pap. 20, 338 (1926) T311; BS J. Research 3, 532 (1929) RP106.

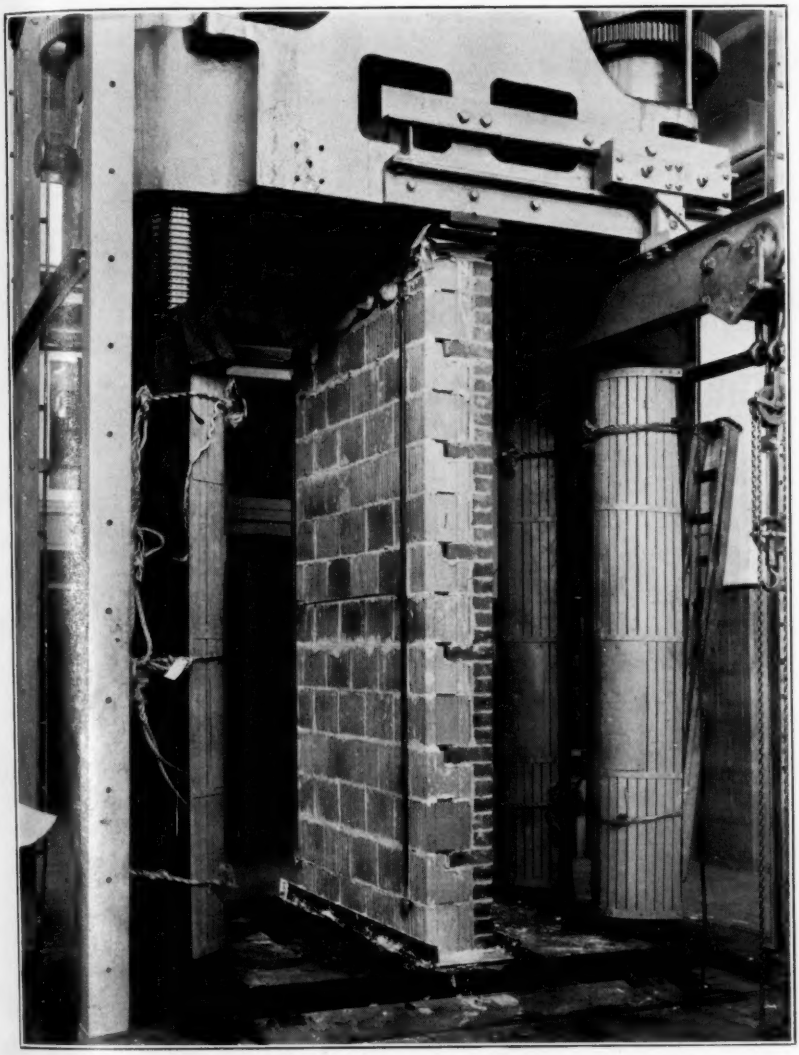


FIGURE 6.—*Wall C–1 in the testing machine ready for compressive test, eccentric loading.*

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(b) BEHAVIOR UNDER LOAD

The mortar in the bed joints of the tile backing crushed as the loads approached the maxima. Usually the crushing of the mortar was evident before any other sign of impending failure. This was fol-

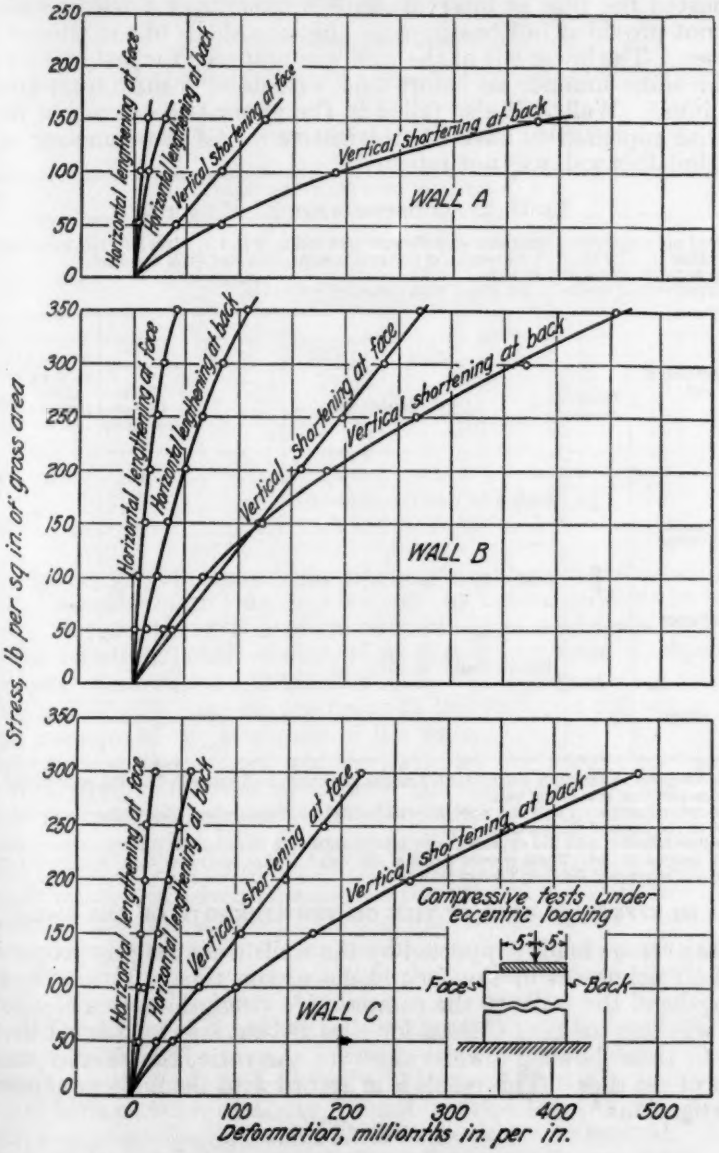

FIGURE 7.—*Stress-deformation relations for the walls.*

lowed by the appearance of vertical cracks in some of the tiles and sometimes by vertical cracks in the header bricks between the facing and backing.

(c) COMPRESSIVE STRENGTH

The compressive strengths of the walls are given in table 2. Wall *C–1* failed when the average stress was 335 lb/in.[2] The damaged portion of the wall was confined to the upper two courses of tile. Upon removing these courses, it was observed that the mason had supported the tiles at intervals with fragments of brick and tile and had not provided full bearings for the face shells of the tiles of these courses. The lower 8 ft of the wall was prepared for test and reloaded in the same manner as before and withstood a maximum stress of 480 lb/in.[2] Wall *A–1* also failed in the upper two courses of tile and likewise appeared to have been defective in the same manner as wall *C–1*, but this wall was not retested.

TABLE 2.—*Compressive strength of the walls.*

Walls of end-construction structural clay tile and brick facing, 9 ft, 3 in. high; 5 ft, 1 in. long; and 12.3 in. thick. Mortar, 1C:0.42L:5.18, by weight, of portland cement, hydrated lime, and sand.
Walls tested at ages of 57 to 62 days.
Compressive load applied at top of wall with eccentricity of 1.15 in.

Designation of wall	Tiles			Weight of walls per unit of face area	Compressive strength[1]
	Designation	Description	Thickness of face shells		
			in.	lb/ft²	lb/in.²
A–1	*A*	6-cell, 8 by 12 by 7½ (standard)	0.75	88	[2] 235
A–2	*A*	6-cell, 8 by 12 by 7½ (standard)	.75	88	326
Average					280
B–1	*B*	6-cell, 8 by 12 by 7½ (thick shells)	1.50	100	653
B–2	*B*	6-cell, 8 by 12 by 7½ (thick shells)	1.50	100	590
Average					620
C–1	*C*	Double shell, 8 by 12 by 7½	1.12	92	[3] 335 or 480
C–2	*C*	Double shell, 8 by 12 by 7½	1.12	92	453
Average					[3] 390 or 465

[1] The compressive strength was calculated as the maximum load supported by the wall divided by the gross cross-sectional area of the wall.
[2] The upper 2 courses of wall *A–1* were not well bedded and fragments of tile and brick were found, after the test, in the joints of these courses.
[3] The first failure of wall *C–1* appeared to be premature and to be caused by defective construction in the upper 2 courses of tile. These courses failed at 335 lb/in.². After removing these courses, the wall was retested and supported 480 lb/in.² before failure.

(d) EFFECT OF KIND OF TILE ON THE STRENGTH OF THE WALLS

The average loads supported by the walls were roughly proportional to the thicknesses of the face shells of the tiles. The ratio of the strengths of the walls to the compressive strengths (gross area) of the tiles was less for tiles *C* than for tiles *B*, and less for tiles *A* than for tiles *C*, thus showing lower values for the ratio, the thinner the face shells of the tiles. This result is in accord with the findings of previous investigations.[5]

2. WALLETTES

(a) BEHAVIOR UNDER LOAD

The crushing of the mortar in the joints was usually the first evidence of impending failure of the wallettes built with mortars 2 and 3. This was followed by the appearance of vertical cracks in the tiles.

[5] J. Research NBS 6, 857 (1931) RP310.

Although the crushing of mortar in tile masonry is not always apparent, even when an examination after failure shows that the mortar has failed, some spalling was noticed with some of the specimens built with mortar 1. Examinations of fragments of mortars 1 and 4 from the joints, after the tests, indicated that the mortars either were abnormally weak or had been partially crushed.

(b) COMPRESSIVE STRENGTH

The results of the compressive tests of the wallettes are given in table 3.

TABLE 3.—*Compressive strength of the wallettes*

Each wallet te consisted of 3 tiles set on end with only the 2 face shells bedded in mortar. Wallettes tested in compression at the age of 2 months

Tile	Mortar	Compressive strength (gross area)				Average compressive strength (bedded area)
		Specimen 1	Specimen 2	Specimen 3	Average	
		lb/fn.²	lb/in.²	lb/in.²	lb/in.²	lb/in.²
A	1	500	435	605	510	2,650
C	1	520	695	610	610	2,160
D	1	1,010	1,655	1,470	1,380	3,900
E	1	520	570	855	650	1,710
F	1	750	810	850	800	2,220
G	1	405	510	445	450	1,200
B	1	1,370	1,110	1,435	1,300	3,440
B	2	705	705	605	670	1,780
B	3	475	530	455	490	1,300
B	4	1,620	1,110	1,350	1,360	3,600

The values of compressive strength (gross area) were obtained by dividing the maximum load on a wallette by the product of the length and width of the tile. The ratios of the strengths of walls *A*, *B*, and *C* to the strengths, respectively, of wallettes with tiles *A*, *B*, and *C* and mortar 1, were 0.55, 0.48, and 0.64. This rather wide range in the ratios indicates that the strengths of the wallettes did not provide a close measure of the strengths of the walls.

Nevertheless, the strengths of the wallettes may provide an indication of relative efficiencies of some of the designs of the tile. Comparing the strengths of the wallettes of tiles of approximately equal weights, it is seen that tiles *D* were more efficient than tiles *B* and tiles *F* than tiles *E*. The splaying of the ends of the shells of tiles *G* apparently was not of advantage as the strengths of the wallettes of tiles *G* were less than for those of the otherwise similar tiles *C*.

As previously mentioned, the curing conditions for the mortar in the wallettes were unfavorable in that the joints were exposed to rapid drying. The small volume of mortar in the wallettes was exposed to the free circulation of air of low relative humidity and, therefore, dried more rapidly than the mortar joints in larger specimens of masonry. Mortar 1, which contained a relatively large amount of a plastic lime putty of high water retentivity, probably dried less rapidly than the others, and, accordingly, hardened at a rate nearer to normal. Under these conditions the strengths of the wallettes probably do not afford reliable estimates of the relative strengths of large specimens of masonry with the four mortars used. The data in Technologic Paper T311 indicate that, for large walls of end-construction tile, the strength of the walls was approximately proportional to the square root of the

compressive strength of the mortar cylinders.[6] Similarly, it has been found that the strengths of solid walls of brick are approximately proportional to the cube root of the strengths of the mortars.[7] In contrast with these results obtained for large walls, the strengths of the wallettes with mortar 4 were only slightly greater than with the much weaker mortar 1. It may be concluded, therefore, that the conditions were relatively not as favorable for the wallettes with mortar 4 as for those with the other mortars which normally develop much lower strengths.

V. CONCLUSIONS

1. Behavior under load of the walls of end-construction tile and brick showed failure of the mortar in the bed joints of the tile before failure of other portions of the walls. This was evidenced by the increasing rate of deformation with increasing loads and by the crushing of the mortar at the back face of the walls.

2. Strengths of the walls were roughly proportional to the thickness of the face shells of the tiles.

3. Average compressive strengths of the wallettes composed of three tiles with their face shells bedded in mortar ranged from 450 to 1,380 lb/in.^{2} of gross cross-sectional area.

4. Crushing of the bed joints was the first sign of impending failure for the wallettes with mortars of masonry cement and sand. Some crushing of these joints was observed also with the cement-lime and the cement mortars. Although the curing conditions for the mortars were believed to be unusually unfavorable, strengths of the wallettes with masonry cement mortars were much lower than for those with the cement-lime mortars.

5. Although there was a marked tendency for the strengths of the wallettes to increase with thickness of the face shells of the tiles, this relation was not as uniform as was found with the data for the walls.

6. Wallettes of the tiles having two oval cores were stronger than those of six-cell tiles of about the same weight. Wallettes of tiles *G*, the ends of the shells of which were splayed to provide a large bearing area, were not as strong as those of otherwise similar tiles *C* of double-shell design.

The Housing Division assisted in defraying the cost of the investigation, and the structural section of that Division, A. M. Korsmo, principal structural engineer, planned the investigation and designed the specimens. The tiles were donated by the National Fireproofing Corporation, and the bricks were donated by the Locher Brick Co.

Acknowledgment is made also of the assistance of C. C. Fishburn, who supervised the construction of the walls, and of Messrs. L. R. Sweetman and C. W. Ross, who assisted in the testing of the walls.

WASHINGTON, December 18, 1936.

[6] Tech. Pap. BS 20, 352 (1926) T311.
[7] J. Research NBS 3, 546 (1929) RP108.

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SIMPLIFIED DETERMINATION OF RESIN IN PAPERS AND PULPS

By Herbert F. Launer

ABSTRACT

A method is given for the simple and precise determination of resin in papers which have been surface-sized with glue or starch, coated with casein-clay emulsion, or not surface-sized or coated. The extracting solution is 95-percent ethyl alcohol acidified with hydrochloric acid in the ratio 4 ml of concentrated HCl: 1,000 ml of alcohol. The extract is dissolved in anhydrous ether, so that the usual laborious and time-consuming washing of the ether solution with water to eliminate the nitrogenous sizing or coating materials is avoided. The method is applicable also to the determination of natural resins in wood pulps. The equivalent weight of the extracted resin, based on the oxidation by dichromate, is made the basis for a new criterion of the purity of the extract.

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I. INTRODUCTION

The method in general use at present for the quantitative determination of resin [1] is that of the Technical Association of the Pulp and Paper Industry, known as TAPPI tentative standard T408m, and referred to subsequently as the TAPPI method in this paper. In this method the extracting solvent is acidulated alcohol (95-percent alcohol, 90 percent; glacial acetic acid, 0.5 percent; water, 9.5 percent; by volume). If nitrogenous materials are present in the paper, the alcoholic solution must be evaporated to dryness and the residue extracted with ether. This ether solution of resin must then be washed with two or more portions of water. If no nitrogenous materials are present, the alcoholic solution is simply evaporated to dryness and the residue weighed as resin.

[1] In this article both natural resins occurring in wood pulps and rosin added to the paper will be referred to as "resin", unless the specific instance requires a distinction to be made.

Since the TAPPI method was used in the present work for purposes of comparison only on materials containing no surface-sizing or coating, such as glue, starch, or casein, the ether extraction was omitted. The alcoholic extracts were filtered, however, the omission of which process constitutes an obvious shortcoming of the TAPPI method. Furthermore, the time of extraction was extended to 2 hours at the rate of 15 siphonings an hour, which is much more than the TAPPI method calls for.

Extraction by the TAPPI method has been shown by Sutermeister and Torrey[2] to be incomplete. They developed a method in which they recommended the use of a solution of the composition 25 ml of concentrated sulfuric acid to 1,000 ml of 95-percent ethyl alcohol, and used a preliminary 5-hour period of steeping, and an 8-hour period of actual extraction.

II. ACIDITY OF THE SOLVENT AND THE TREATMENT OF THE ALCOHOLIC EXTRACT

The function of the acid is to resolve the aluminum-rosin aggregate into its components, thus allowing the rosin to dissolve in the alcohol. According to the work of Sutermeister and Torrey, acetic acid does not furnish sufficient hydrogen ion to accomplish this, which is in accord with the findings of the present work. The use of sulfuric acid requires, however, the long steeping and extraction periods, both of which are somewhat impractical for the routine analysis of large numbers of samples. When sulfuric acid is used, the steeping and long extraction seem to be necessary for the reason that the acid is nonvolatile under the conditions of extraction, and is soon almost completely washed out of the siphon cup. It was found in this laboratory that the sulfuric-acid concentration, initially $0.9M$, decreases to $0.001M$ in the siphon cup after the first half hour of distillation, when measured with a glass electrode in the presence of the paper.

To obviate these difficulties the strong volatile hydrochloric acid was used in the present work. By the use of this acid the extraction, without preliminary steeping, was found to be practically complete in 2 to 2½ hours. Furthermore, the partial neutralization of the acid before evaporation of the solvent, necessary when sulfuric acid is used, is not necessary when hydrochloric acid is the acidulant, because this acid evaporates along with the alcohol without becoming sufficiently concentrated to attack the resinous material significantly. This was found by separate experiments in which rosin of known weight in alcoholic hydrochloric acid was evaporated to dryness, dissolved in ether, reevaporated, and weighed. The change in weight was negligible when compared with that of the control experiment, in which no acid had been used.

In the present work the simple "Underwriter" equipment was used. When the strongly acidic solution recommended by Sutermeister and Torrey was employed under these conditions, large quantities of the products of the hydrolysis of cellulose were formed which had to be separated from the resin by the usual water-washing of the ether extract in separatory funnels. To avoid this, it was necessary to use a lower acidity, which would have to be higher than that of the TAPPI solvent, however, to allow acceptably complete extraction.

[2] E. Sutermeister and W. V. Torrey, Paper Trade J. 94, 33 (January 21, 1932).

A concentration of hydrochloric acid in the alcoholic solvent, favorable from the standpoints just discussed, was arrived at in the following manner.

The acidity of the TAPPI solvent in the siphon cup was measured with the glass electrode. The hydrogen-ion concentration (more exactly, the activity, calculated directly from the observed pH) was found to be 0.00003*M*. Accordingly, an acidity range above 0.00003*M* was investigated. It was found by trial that a 0.4-percent (by volume) solution consisting of 4 ml of concentrated (35 to 37 percent) HCl and 1,000 ml of 95-percent ethyl alcohol gave maximum extraction of resin with minimum extraction of other substances. A 1.2-percent alcoholic hydrochloric acid solution yielded no more resins, but gave a much larger amount of the hydrolysis products of cellulose, which made subsequent steps more difficult. An 0.08-percent solution gave incomplete extraction (90 percent) on papers. The pH of the siphon-cup distillate from the 0.4-percent solution was found to be 2.2, corresponding to an acidity of 0.006*M*.

Finally, the alcoholic extract often contains, along with the resin, finely divided foreign matter. This is best coagulated by dehydration through brief heating of the residue in the drying oven. After this treatment, the resin dissolves readily in the anhydrous ether, and the material which goes into suspension settles out on short standing. The ether solution is then easily filtered.

III. NEW METHOD OF EXTRACTION IN DETAIL

Five to seven grams of the paper or pulp is cut into strips approximately 5 by 40 mm and placed lengthwise into the Underwriter siphon cup. The extracting solution is made up in the ratio 4 ml of concentrated 35 to 37 percent reagent grade HCl:1,000 ml of 95-percent ethyl alcohol. The hydrochloric acid may be omitted in the case of wood pulps.

The extraction process is continued for approximately 2 hours at the rate of 15 siphonings an hour (equal to 500 ml in the apparatus used) for uncoated and nonsurface-sized papers and pulps, and for 2½ hours when glue, starch, or casein is present. The alcoholic solution is evaporated to dryness, preferably on a steam bath, until acrid odors are no longer noticeable. The residue is then heated in a drying oven at 100° C for 15 minutes. After cooling, 20 ml of anhydrous ether is added. The resinous material dissolves very rapidly (5 to 30 seconds) but care should be taken that none remains covered by foreign materials. After standing 15 to 20 minutes to further the coagulation and settling out of the foreign matter, if necessary, the ether solution is filtered with suction through a fine-pore filter paper cut to fit a Gooch crucible, directly into a weighed beaker. It is usually necessary to refilter the filtered solution through the same paper. Another 20-ml portion of ether is used for rinsing. The ether is conveniently evaporated under reduced pressure with the beaker placed in water at 40° C. Fifteen minutes in the drying oven at 100° C will then suffice to remove moisture. Still more rapid, however, is evaporation in a strong current of air, after which the drying time must be lengthened to 30 minutes, as water is condensed from the air by cold ether. The residue is then weighed to the nearest milligram.

If the paper contains fillers, such as ZnS, $CaSO_3$, and $CaCO_3$, that react with acids, the sheet, previously weighed, is dipped into normal

aqueous hydrochloric acid solution and allowed to drain for 5 minutes. It is then placed upon a suitable surface and washed free from acid with tap water. After drying, the paper is cut into strips and extracted in the manner just described.

IV. EXPERIMENTAL RESULTS AND DISCUSSION

1. EQUIVALENT WEIGHT OF THE EXTRACT

It became necessary to test the extracts for the presence of probable foreign substances, such as clay or other inorganic salts, including those soluble in water, the products of the hydrolysis of cellulose, and coating and surface-sizing materials, such as glue, starch, and casein. It was found that a suitable test was the oxidimetric equivalent weight, which is simply the number of grams of the extract which will reduce one equivalent, 49.03 g=1/6 mole, of potassium dichromate, $K_2Cr_2O_7$. The actual completeness of the reaction, that is, whether or not all carbon is oxidized to carbon dioxide, was not investigated extensively, except that acceptable checks were obtained with known weights of various grades of rosin. The equivalent weight of a sample of papermakers' rosin, grade *F*, in the form of an emulsion prepared in the National Bureau of Standards paper mill by saponification with hot sodium carbonate and subsequent dilution, was determined as follows:

5.00 ml of emulsion was neutralized with 0.4-percent alcoholic hydrochloric acid, an excess of the latter was added, and the mixture evaporated to dryness on the steam bath. After further drying for 15 minutes in an oven at 100° C and cooling, the rosin was extracted with anhydrous ether. This solution was evaporated, the residue dried as before, cooled and weighed. Twenty-five ml of concentrated sulphuric acid was then poured over the rosin and allowed to stand 1 hour with frequent agitation. The rosin dissolved without oxidation, as shown by separate experiments wherein the time of standing was increased tenfold with negligible change in the equivalent weight of the rosin. The solution was slowly poured into a 400-ml beaker containing 30.00 ml of standard 1.835*N* potassium dichromate solution, 25 ml of additional sulphuric acid was added, followed by 20 ml of water, and the solution was kept at 150 to 155° C for 20 minutes, air being constantly bubbled through it to prevent bumping. The solution was then diluted twofold, cooled to 60° C or lower, and the remaining dichromate determined electrometrically with ferrous ammonium sulphate.

The results with this method are shown in table 1.

TABLE 1.—*Equivalent weight of a sample of papermakers' rosin, grade F, after saponification*

Weight of rosin	Volume 1.835*N* dichromate used	Equivalent weight
g	ml	g
0.159	24.1	3.60
.160	24.3	3.57
.160	23.5	3.71
	Average.	3.63

The value 3.63 is in good agreement with the equivalent-weight values of the extracts from all types of papers studied (see table 5). An extract is thus considered "pure" in this work if its equivalent weight is approximately 3.6.[3] All of the impurities listed above would raise this value. Clay, if present to the extent of 10 percent in the extract, would raise it to 4.0. Cold or hot water-soluble materials found by the writer to be present to 1.1 to 1.2 percent in the soda and sulfite pulps studied, and found to have equivalent weights of 10.1 and 9.0, would obviously raise the value. The same applies to the hydrolysis products of cellulose, which have an equivalent weight of 6.8,[4] the same, of course, as cellulose. Finally, starch has the same value as cellulose, whereas the glue and casein used in the papers have equivalent weights of 7.1 and 5.7, respectively, both of which were experimentally determined in this laboratory.

2. PULPS AND THE UNCOATED AND NONSURFACE-SIZED PAPERS

(a) PAPER STOCK WITH KNOWN AMOUNTS OF ROSIN

A purified sulfite pulp, known on the market as "alpha pulp", was beaten for 3 hours in a semicommercial beater in the National Bureau of Standards' paper mill. More water was then added until the weight of the stock constituted 2.5 percent of the whole. The mixture was then stirred for 1 hour, after which 10.00 ml of analyzed[5] rosin emulsion, prepared in the same paper mill by the usual process, was pipetted in and stirred for 1 hour. Alum solution was then added until the pH became 4.1. After the mixture had been stirred 1 hour more it was filtered on a large Büchner funnel, dried, cut into three equal piles of strips, and analyzed for rosin by the new method. The filtrate, 700 ml., was acidified and the rosin determined by extraction with ether. A like quantity of pulp was dried and analyzed for natural resins.[6] The results are given in table 2.

TABLE 2.—*Analytical data for paper stock with known amounts of rosin*

Rosin added (g)			0.3490
Natural resins (g)			.0087
Total (g)			.3577
Rosin in filtrate (g)			.0245
Resins in fibers (g)			.3332
Weight of dry cake (g)			17.40
Therefore, resins in cake (%)			1.92
Portions taken for analysis (g)	5.38,	5.82,	6.20
Resins recovered (g)	.1020,	.1095,	.1170
Therefore, resins found (%)	1.90,	1.88,	1.89
Average (%)			1.89

It is seen from the values for the resin present, 0.3332 g, and the resin found, 0.3285 g, that the recovery is 98.5 percent.

[3] A much paler and better grade of rosin was found to give the equivalent-weight values of 3.38, 3.32, 3.34; average 3.35.

[4] This was determined as follows: Sulfite paper in a siphon cup was steeped overnight in a 3.9-percent alcoholic solution of hydrochloric acid. The usual process for resin extraction was then carried out, but with this solution, after which the alcoholic solution was filtered, evaporated to dryness, weighed, and the equivalent weight determined. The tarry residue was found to be 8.2 percent, by weight, of the paper sample. The residue was then oxidized with dichromate as usual.

[5] The rosin emulsion was analyzed as follows: 5.00 ml of emulsion was pipetted into a separatory funnel containing ether and dilute hydrochloric acid, and shaken. It was washed once more with very dilute hydrochloric acid, the aqueous portions being extracted with fresh portions of ether. Duplicate determinations gave 0.175 and 0.174 g; average 0.1745 g of resin per 5 ml of emulsion. This analysis was carried out 10 weeks prior to the one described in the preceding section.

[6] The new method was used for the determination of this small quantity. An error of 100 percent in this value would result in an error of only 0.05 percent in the resin content of the cake. However, errors inherent in the determination of this quantity would cancel, provided that the same method of analysis is used both for the sized and unsized cakes.

(b) COMPARISON WITH THE RESULTS OF OTHER METHODS ON VARIOUS PULPS AND PAPERS

The results of the tests are recorded in table 3. The percentage was calculated on the basis of the oven-dry weight of each material. The materials used were no. 1018, a soda pulp; no. 1017, a sulfite pulp; no. 1014, a paper made from old white rags; and no. 879, a paper made from sulfite pulp. The numbers refer to papers used for other experiments.[7] The concentration of acids used is expressed in volume-percent.

TABLE 3.—*Analytical results on pulps and uncoated and unsurface-sized papers*

	New method (0.4% hydrochloric) acid)		TAPPI method (0.5% acetic acid)		Absolute alcohol (unacidified)		Sutermeister and Torrey (2.5% sulphuric acid)	
	Resin	Equivalent weight	Resin	Equivalent weight	Resin	Equivalent weight	Resin	Equivalent weight
	Percent	*g*	*Percent*	*g*	*Percent*	*g*	*Percent*	*g*
NO. 1018. SODA PULP								
	0.18	3.49	0.50	6.38	0.34	4.88		
	.19	3.87	.51	7.09	.32	4.55		
			.49	6.60				
Average	.18	3.68	.50	6.71	.33	4.71		
NO. 1017. SULFITE PULP								
	0.72	3.54	1.06	4.96	0.86	3.65	0.73	3.65
	.73	3.70	1.01	4.96	.82	3.93	.75	3.60
			1.00	4.80	.80	3.55	.72	3.60
Average	.72	3.62	1.02	4.91	.83	3.71	.73	3.62
NO. 879. SULFITE PAPER								
	2.46	3.57	2.40	3.71	1.76	3.65	2.56	3.73
	2.56	3.73	2.43	3.76	1.77	3.49	2.56	3.64
	2.49	3.62	2.57	4.04	1.80	3.44		
Average	2.50	3.64	2.47	3.82	1.78	3.55	2.56	3.68
NO. 1014. RAG PAPER								
	1.92	3.67	1.71	3.65			1.92	3.64
	1.89	3.57	1.88	3.71			1.90	3.52
	1.90	3.62	1.88	3.65				
Average	1.90	3.62	1.82	3.67			1.91	3.58

The percentages of resin in the pulps determined by the TAPPI method, column 4, are much higher than those found by the other methods, columns 2, 6, and 8. This is due to the fact that the TAPPI extract contains impurities which are carried down by the rather large amount of water present (14 percent), and also by the alcohol. These impurities are not only visible and impart an inhomogeneous and "dirty" appearance to the residues, but also reveal themselves in the high equivalent weights reported in column 5. That a large part of the impurity is due to water is shown by the lower results with a nonaqueous solvent, column 6.

[7] R. H. Rasch, M. B. Shaw, and G. W. Bicking, BS J. Research 11, (1933) RP574.
M. B. Shaw, G. W. Bicking, and M. J. O'Leary, J. Research NBS 14, 649 (1935) RP794.

The failure of the TAPPI method arises from the fact that all alcoholic solvents also extract materials that are nonresinous, as shown by their insolubility in ether. This is further shown in a consideration of the results with the sulfite paper.

The percentages of resin in the papers, columns 2, 4, 8, using the three acidified solvents are in good agreement. The reason for this apparent contradiction of the findings of Sutermeister and Torrey [8] that the TAPPI extraction is incomplete, is immediately indicated by the appearance of the TAPPI residues and by their somewhat high equivalent weights, column 5, showing that impurities are present. This is definitely shown by the following experiments: The extractions by the new method and the TAPPI method were carried out on the sulfite paper. The weighed residues were dissolved in ether, which was then washed with water in separatory funnels, evaporated, dried, and weighed. The paper from which the resin had supposedly been extracted by each method was then subjected to a second extraction, but this time by the new method. The results are listed in table 4 and show clearly that the TAPPI solvent fails to extract all of the resin in papers, and that water-soluble impurities are extracted. The results also show that the extracts by the new method contain negligible amounts of water-soluble materials, and that the extraction is practically complete.

TABLE 4.—*Effect of washing the residues obtained by the new and TAPPI methods*

[The results of second extraction on the sulfite paper]

Method	Resin percentage		
	Resin not washed with water	Resin washed with water	Second extraction on paper by the new method
New	2.47	2.44	0.02
	2.55	2.53	.00
	2.46	2.44	.02
Average	2.49	2.47	.01
TAPPI	2.42	2.17	0.20
	2.46	2.20	.17
	2.59	2.25	.25
Average	2.49	2.21	.21

Extraction by the method of Sutermeister and Torrey [9] gave the results listed in column 8 of table 3, which were obtained by using an Underwriter siphon cup, a period of steeping overnight, and a 5-hour period of extraction. The results are in good agreement with those of the new method, which has the advantage of being far shorter and simpler, without sacrifice of accuracy.

3. COATED AND SURFACE-SIZED PAPERS

Further test of the new method showed that the results were not affected by the presence of surface-sizing or coating materials. Ordinarily, the presence of such materials necessitates laborious and time-consuming washing of the ether extracts with water.

[8] E. Sutermeister and W. V. Torrey, Paper Trade J. **94**, 33 (January 21, 1932).
[9] See footnote 8.

All of the results listed in table 5 were obtained by the new method. The materials used were the same two papers described in section IV–2–b, p. 232, but surface-sized or coated, either in the Bureau of Standards paper mill as in the case of no. 1014—glue, or by hand in the laboratory, employing procedures[10] in use at this Bureau.

TABLE 5.—*Analytical results with surface-sized and coated papers, using alcoholic hydrochloric acid (4:1,000)*

Kind of coating or surface sizing	No. 879 sulfite paper			No. 1014 rag paper		
	Amount of coating	Resin	Equivalent weight	Amount of coating	Resin	Equivalent weight
	Percent	Percent		Percent	Percent	
None [a]		2.50	3.64		1.90	3.62
Glue	4.1	2.38		1.6	1.87	
	4.0	2.43		1.6	1.90	
	4.0	2.49		1.6	1.83	
Average		2.43	3.58		1.87	3.56
Starch	4.0	2.45		3.5	1.91	
	4.0	2.38		4.0	1.84	
	4.0	2.37		4.0	1.86	
Average		2.40	3.60		1.87	3.62
Casein [b]	1.5	2.48		1.6	1.94	
	1.6	2.57		1.7	1.98	
	1.5	2.51		1.8	1.92	
Average		2.52	3.56		1.95	3.62

[a] Results for the untreated papers were taken from table 3.
[b] The amounts of casein do not include the clay, which was approximately 10 percent.

If fillers, such as ZnS, $CaSO_3$, and $CaCO_3$ are present in paper, the acidity of the extracting solvent is changed unless the filler is first removed by dipping in normal hydrochloric acid, washing and drying. Such treatment was found not to affect the resin content of the paper.

WASHINGTON, December 18, 1936.

[10] For casein see Ind. Eng. Chem. 25, 904 (1933). For glue and starch see footnote 7.

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PERMEABILITY TO MOISTURE OF SYNTHETIC RESIN FINISHES FOR AIRCRAFT

By Gordon M. Kline

ABSTRACT

The permeability to moisture and some related properties of various synthetic resin finishes used on aircraft are reported. The glyceryl-phthalate enamels are less permeable to moisture under relatively dry conditions than are the enamels made with a phenol-formaldehyde resin. This order is reversed, however, under wet conditions. This corresponds with the service uses to which these finishes have been found to be best adapted. The aircraft finish made with a cellulose nitrate base is much more permeable to water vapor under both wet and dry conditions than are the resinous materials. The permeability of these finishes is not directly proportional to the vapor-pressure difference. The rate of passage of moisture per unit difference in vapor pressure increases with rising temperature. A given type of aircraft finish transmits moisture at the same rate whether in contact with liquid water or with saturated water vapor. The mechanism of penetration is, therefore, probably the same in the two cases. The film probably behaves as a typical colloidal, permeable membrane, and the water vapor is adsorbed by it and transmitted through the film by a process of chemical diffusion. Some observations on the absorption of moisture by resinous films and the effect of carnauba wax on permeability are presented. Results of measurements of the permeability to moisture of gas-cell fabrics of varying gelatin content and amount of paraffin coating are also given.

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I. INTRODUCTION

The permeability to moisture of a protective coating is now recognized as a fundamental property of practical importance in connection with its use over metals. The presence of moisture is necessary for the common types of metal corrosion. The problem of protecting

the metal is not merely one of waterproofing, since a sound coating does not normally allow the passage of water by diffusion through holes or capillary spaces. The films behave rather as typical colloidal, permeable membranes, according to the data obtained in this investigation. Water vapor is adsorbed by them and transmitted through the films by a process of chemical diffusion.

This process is closely analogous to the passages of gases through films of rubber, which was the subject of a previous investigation at the National Bureau of Standards [12].[1] Gases are adsorbed on one surface of the rubber, diffuse through it, and evaporate from the other side. Water vapor, which is of greater density than gaseous hydrogen, passes through it about fifty times as fast. Likewise, water vapor is adsorbed to a much greater extent by rubber than is hydrogen. The rate of passage of a gas through rubber is proportional to the difference in pressure or partial pressure of the gas on the two sides of the film. The rate also increases with increase in temperature and decreases with increase in thickness of the film.

Organic film-forming materials, such as synthetic resins, drying oils, and cellulose derivatives, differ markedly in their affinity for water. Regenerated cellulose and gelatin are known to be very hygroscopic, and films prepared from these substances are characterized by high rates of passage of moisture through them. On the other hand, the hydrocarbon waxes, such as the paraffins, have very little attraction for water, and act as moisture-proofing coatings for many commercial purposes. The synthetic resins differ among themselves in hygroscopicity. The styrene and vinyl types, which are essentially hydrocarbons, absorb only negligible amounts of water; the glyceryl phthalates, which are of the ester type and oxygen-bearing compounds, will absorb considerable amounts of moisture. Paints prepared with resinous vehicles of various types will yield films which show different rates of absorption and diffusion of moisture.

This paper describes the results of a study of the permeability to moisture and some related properties of various aircraft finishes used by the Navy Department.

II. EXPERIMENTAL PROCEDURE

1. PREPARATION OF THE FILMS

Films were prepared for this work by dipping amalgamated tinplate panels in the respective aircraft finishes, the compositions of which are described in table 1. The tin plate, 0.016 inch thick, was cleaned with toluene, dried, and covered with mercury. The surface was rubbed gently with a silk cloth to obtain complete amalgamation. Clean mercury was then poured over the surface of the plate and the excess allowed to drain off. In this way a plate having a smooth, polished appearance was produced. This amalgamated plate was dipped within 1 hour of its preparation into the coating material and supported in a vertical position to allow the excess of liquid to flow off. The first coat was dried 1 week before application of further coats because of a tendency for the films to creep if insufficiently dry. This is caused by the lack of adhesion to the amalgamated tin. Three-day intervals between any additional coats were found to be ample to assure against creeping. After the desired number of coats

[1] Figures in brackets refer to literature citations listed at the end of this paper.

TABLE 1.—*Composition by weight of aircraft finishes studied*

Specification	Product on wet basis		Nonvolatiles			Volatiles	
			Resinous vehicle		Pigment		
	Nonvolatile (minimum)	Volatile (maximum)	Type	Amount		Type	Amount
	%	%		%	%		%
V-11B	44	56	Glyceryl-phthalate Modifying agents	Min 40 Max 60	None	Aliphatic and terpene hydrocarbons.	100.
E-5 (gray)	50	50	Same as above	Approx 50	Approx 50	do	100.
E-6B (black; type *I*)	33	67	Same as above	Min 90	Max 10	do	100.
V-10A	60	40	(33 gallon length) Bakelite *XR254* China wood oil Castor oil Linseed oil Drier	 Min 28 Min 45 Min 2 Max 25 As required	None	Butyl alcohol Turpentine Dipentine Mineral spirits	Min 5. Min 10. Min 10. Max 75.
E-4A (orange yellow)	60	40	Same as above	Min 48	Min 48	Same as above	Same as above.
M-67D (gray)	60	40	Same as above	Min 48	Min 48	Same as above	Same as above.
P-83B	65	35	Same as above	Max 42	Min 58	Same as above	Same as above.
P-24A	40	60	Bakelite *XR3962*	Max 67	Min 33	Toluene	100.
P-27	60	40	Bakelite *XR3962* Glyceryl-phthalate	Max 45	Min 55	Butyl alcohol Hydrocarbons	Min 10. Max 90.
L-8D (gray)	41	59	Cellulose nitrate Glycol sebacate Glyceryl-phthalate	Approx 24.4 Approx 24.4 Approx 12.2	Approx 39.0	Esters (as Et. Ac.) Alcohols (bp. above 115°) Alcohols (bp. below 115°) Aromatic hydrocarbons	Min 40. Min 14. Max 6. Max 40.

had been applied, the films were loosened at the edge with a razor blade and stripped from the panel with the aid of a steel spatula. Disks approximately 72 mm in diameter were cut from the films for the permeability tests, and their average thickness was determined with a dial gage.

2. MEASUREMENT OF PERMEABILITY TO MOISTURE

The rate of transfer of moisture through paint films, wrapping materials, and other membranes has been measured by a number of investigators. Selected literature references on this subject are appended. The method has been gravimetric in nearly every case, but the procedures have varied considerably. The following method

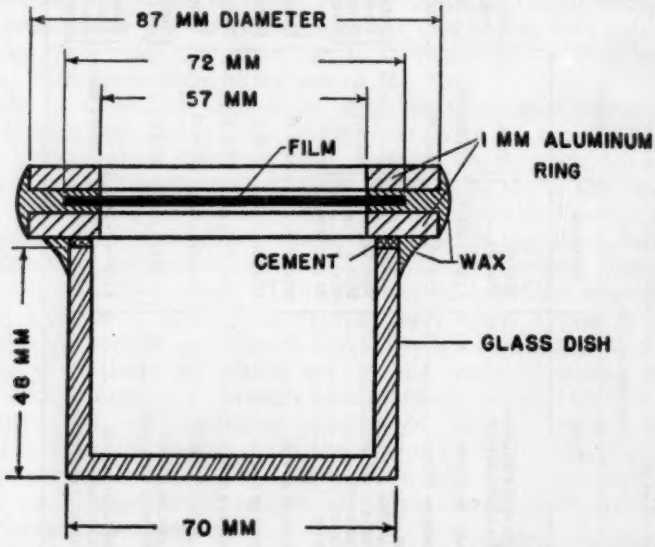

FIG. 1.—*Diagram of cell used for measurement of permeability to moisture.*

is a convenient one and gives results which are comparable with many of the published data.

The film to be tested is sealed on a glass dish, containing phosphorus pentoxide, water, or a saturated salt solution which will produce the desired relative humidity inside the cell (fig. 1). The chemicals used are shown in table 2, together with the calculated vapor-pressure differences between the two sides of the films in the tests. The cells are placed in a cabinet in which the temperature and relative humidity are controlled and are then weighed on a Chainomatic analytical balance at approximately 3-day intervals until a constant for the moisture permeability has been established. Glass crystallizing dishes known as Tanners Special were used for the cells. These dishes are 70 mm in outside diameter, 50 mm deep, and weigh approximately 35 g. A rough-ground rather than a fire-polished edge is to be preferred on these dishes. An aluminum ring of 57 mm inside diameter and 87 mm outside diameter was fastened to the rim of the dish with Cementyte of hard grade. A melted mixture of equal parts of beeswax and rosin was used to seal the outer edge of the dish

to the metal and to close any cracks between them. The disk cut from the film was attached to another aluminum ring with the beeswax-rosin mixture and subsequently sealed to the aluminum ring on the cell with the same material. This served to limit the exposed area of the film between the two rings to 25.5 cm ^{2} and to prevent edge leakages.

TABLE 2.—*Reagents used to obtain various relative humidities*

Chemical	Temperature	Relative humidity	Vapor pressure	Vapor-pressure difference between cell and cabinet
	°F	*Percent*	mm Hg	mm Hg
H_2O	70	100	18.77	6.6
KNO_3	70	94	17.6	5.4
$NH_4H_2PO_4$	70	93	17.5	5.3
NaCl	70	76	14.3	2.1
Cabinet	70	65	12.2	
$MgCl_2$	70	33	6.2	6.0
P_2O_5	70	0	0	12.2
H_2O	85	100	30.75	8.9
KNO_3	85	92	28.3	6.5
$NH_4H_2PO_4$	85	93	28.6	6.8
NaCl	85	75	23.1	1.3
Cabinet	85	71	21.8	
$MgCl_2$	85	32	9.8	12.0
P_2O_5	85	0	0	21.8
H_2O	100	100	49.16	14.3
KNO_3	100	90	44.2	9.3
$NH_4H_2PO_4$	100	93	45.7	10.8
NaCl	100	75	36.9	2.0
Cabinet	100	71	34.9	
$MgCl_2$	100	31	15.2	19.7
P_2O_5	100	0	0	34.9

III. PERMEABILITY TO MOISTURE OF FILMS OF VARIOUS AIRCRAFT FINISHES

The amounts of moisture transmitted by the aircraft finishes listed in table 1 were determined for different film thicknesses at various temperatures and relative humidities. The variation in the thickness of a film was about ± 0.1 mil. The values obtained for permeability in grams per hour, as determined by weighing the cells at intervals of 3 to 4 days, varied within approximately ± 2.5 percent of the average; the reproducibility with different films was approximately ± 5 percent. In order to readily compare the results obtained with the different materials, the rate of transmission of moisture for 1 mil thickness was calculated. The assumption was made that the permeability is inversely proportional to the thickness. These calculated values are presented in table 3. The materials are listed in the table in the approximate order of increasing permeability as determined at the three different temperatures.

The exposure environment in which the cell contains water-saturated air on the inside will be referred to as the wet condition; when the air in the cell is dried with phosphorus pentoxide and moisture is transferred through the film from the outside air, which is 65 to 71 percent saturated, the exposure environment will be designated as the dry condition. It will be noted that two of the three primers studied, namely, *P–27* and *P–24*, are less permeable to moisture under both wet and dry conditions than are the remaining finishes. The

glyceryl-phthalate enamels are less permeable to moisture under dry conditions than are the enamels made with a phenol-formaldehyde resin (Bakelite *XR–254*); this order is reversed, however, under wet conditions, the three phenol-formaldehyde films becoming less permeable than the glyceryl-phthalate type. This corresponds with the service uses to which these finishes have been found to be best adapted. Thus, the phenol-formaldehyde finishes are used on parts which come in contact with water, such as hulls, fuselages, etc., whereas the glyceryl-phthalate materials are applied to the external superstructure which is above the water line. The aircraft finish made with a cellulose nitrate base, *L–8*, is very permeable to water vapor under both wet and dry conditions. In service this material is used only for insignia overdoped surfaces.

TABLE 3.—*Permeability to moisture of aircraft finishes calculated to films 1 mil thick and listed in the approximate order of increasing permeability*

Material	Relative humidity in cell	Permeability at—					
		70° F and 65-percent relative humidity		85° F and 71-percent relative humidity		100° F and 71-percent relative humidity	
	Percent	g/hr/m²	g/hr/m²/mm Hg	g/hr/m²	g/hr/m²/mm Hg	g/hr/m²	g/hr/m²/mm Hg
P–27	0	0.41	0.03	0.93	0.04	1.46	0.04
P–24	0	.70	.06	1.40	.06	2.40	.07
E–6	0	.67	.05			3.22	.09
E–5	0	.90	.07	1.75	.08	2.59	.07
M–67	0	1.06	.09	2.09	.10	3.28	.09
P–23	0	.86	.07	2.11	.10	4.08	.12
E–4	0	.98	.08	2.29	.11	4.74	.14
V–11	0	1.40	.11	3.29	.15	6.82	.20
V–10	0	1.47	.12	3.39	.16	7.11	.20
L–8	0	2.37	.19	5.30	.24	17.14	.49
P–24	100	.44	.07	.83	.09	2.36	.17
P–27	100	.73	.11	1.33	.15	3.45	.24
E–4	100	.79	.12	1.44	.16	3.46	.24
P–23	100	.88	.13	1.59	.18	3.26	.23
M–67	100	.94	.14	1.62	.18	3.50	.24
E–6	100	1.07	.16			4.90	.34
V–10	100	1.10	.17	2.01	.23	4.85	.34
V–11	100	1.41	.21	2.46	.28	5.75	.40
E–5	100	1.89	.29	3.15	.35	6.19	.43
L–8	100	4.53	.69	7.68	.86	15.32	1.07

The clear varnishes, phenol-formaldehyde base *V–10* and glyceryl-phthalate base *V–11*, showed the same reversal of permeability under wet and dry conditions, respectively, as the pigmented finishes prepared from them. Films with aluminum powder added to these varnishes were not studied, but the effect of this pigment has been determined and reported in a series of papers from the Aluminum Research Laboratories. They report that the permeability decreases regularly with increase in the concentration of aluminum powder and that in aluminum paints of the same pigment concentration the moisture permeability decreases as the mesh size of the powder decreases or the number of flakes per unit volume of film increases, until the moisture-proofing effect of the flakes eventually approximates that of a granular pigment. They attribute the beneficial effect of aluminum powder to the structure presented by overlapping flakes, which greatly increases the diffusion path.

IV. FACTORS INFLUENCING THE RATE OF PASSAGE OF MOISTURE THROUGH THE FILMS

1. VAPOR-PRESSURE DIFFERENCE

The vapor-pressure difference is determined from the temperature and relative humidity of the atmospheres on the two sides of the film. It can be varied experimentally either by raising or lowering the temperature or by using various reagents to obtain a range of relative humidities. The effect of vapor-pressure difference on moisture transmission of the various coating materials is shown in tables 3 and 4, in which the permeability, expressed as grams per hour per square meter, have been converted to grams per hour per square meter per millimeter of mercury by dividing by the differences in vapor pressure recorded in table 2. It was found that when the temperature is constant and the relative humidity varied, the permeability is not directly proportional to the vapor-pressure difference. In the case of the materials which have low permeabilities, the values found at relative humidities below 75 percent are approximately constant; likewise those from 75 to 100 percent give a constant which, however, is somewhat greater than for the lower relative humidities. For films of cellulose nitrate lacquer which are much more permeable to moisture, the rates of transmission are not at all proportional to vapor-pressure differences, but increase more rapidly than the vapor-pressure difference as the relative humidity is raised. These results partially confirm the conclusions reached by Charch and Scroggie in an investigation of the permeability to water vapor of cellulose wrapping materials. They found that the permeability of a given type of sheet is directly proportional to the vapor-pressure difference existing during the test only when the materials are reasonably impermeable and then only at a relative humidity well below saturation.

2. TEMPERATURE

The effect of raising the temperature at which the test cell is exposed is shown in tables 3 and 4. The permeability in grams per hour per square meter is, of course, greater, since the vapor-pressure difference is increased. Moreover, the permeability per unit-pressure difference is also increased with rising temperature. It will be noted that a greater spread exists between the experimental results obtained with the various types of films at 100° F than at the lower temperatures. For this reason it is preferable to study the various materials at the higher temperature, which is not in excess of conditions to be met in service. This temperature is not sufficient to cause the resinous films to break down during the period of the test, as was shown by determinations of moisture permeability at 70° F after conclusion of the 100° F exposures. The rates measured at such time duplicated those measured initially at 70° F on the same films.

3. TIME

A certain length of time is required for water vapor to diffuse uniformly through the film and set up a steady state of emission from the drier side. This equilibrium was very quickly attained with the materials investigated. However, the cells were kept at least 48 hours under the test conditions before the first weighing was made.

TABLE 4.—*Effect of varying vapor-pressure difference on the permeability to moisture of films of aircraft finishes*

Relative humidity in cell	Permeability at—					
	70° F and 65-percent relative humidity, calculated for 1 mil thickness		85° F and 71-percent relative humidity, calculated for 1 mil thickness		100° F and 71-percent relative humidity, calculated for 1 mil thickness	
Percent	g/hr/m²	g/hr/m²/mm Hg	g/hr/m²	g/hr/m²/mm Hg	g/hr/m²	g/hr/m²/mm Hg
COATING *V-11*						
0	1.20	0.10	2.97	0.14	6.26	0.18
32 to 33	.72	.12	1.74	.15	3.51	.18
75 to 76	.38	.18	.34	.26	.83	.41
93	1.10	.21	1.68	.25	3.72	.35
90 to 94	1.04	.19	1.62	.25	3.14	.34
100	1.37	.21	2.47	.28	5.86	.41
COATING *V-10*						
0	1.29	.11	3.02	.14	7.00	.20
32 to 33	.72	.12	1.67	.14	3.39	.17
75 to 76	.34	.16	.28	.22	.65	.32
93	.81	.15	1.20	.18	2.32	.22
90 to 94	.79	.15	1.25	.19	2.51	.27
100	.96	.15	1.87	.21	5.26	.37
COATING *E-4*						
0	1.05	.09	2.44	.11	5.12	.15
32 to 33	.59	.10	1.38	.12	2.72	.14
75 to 76	.22	.10	.22	.17	----------	----------
93	.73	.14	1.09	.16	2.17	.20
100	.74	.11	1.36	.15	3.17	.22
COATING *E-6*						
0	.66	.05	----------	----------	2.75	.08
32 to 33	.28	.05	----------	----------	1.56	.08
75 to 76	.29	.14	----------	----------	1.34	.67
93	.50	.09	----------	----------	2.45	.23
100	.86	.13	----------	----------	4.30	.30
COATING *L-8*						
0	1.75	.14	4.43	.20	----------	----------
32 to 33	1.03	.17	2.49	.21	6.45	.33
75 to 76	.54	.26	.50	.38	1.37	.69
93	2.41	.45	3.66	.54	7.28	.67
100	4.19	.64	6.85	.77	12.22	.86

The age of the film has been found by Edwards and Wray to have an important bearing on the moisture permeability. The results recorded herein were obtained on films which had been air-dried approximately 30 days before starting the tests.

4. COMPARATIVE BEHAVIOR OF LIQUID WATER AND AIR SATURATED WITH MOISTURE

A large number of tests were made to determine whether water in contact with the films would be transmitted at the same rate when in the vapor and the liquid state. The latter condition was obtained by turning the cell upside down. In most cases the rates were observed to be the same within the experimental error, as indicated in table 5.

TABLE 5.—*Comparative permeability of films of aircraft finishes to liquid water and to saturated water vapor*

Film thickness	Exposure environment in cell S=saturated water vapor; W=liquid water	Permeability at— 70° F and 65-percent relative humidity	85° F and 71-percent relative humidity	100° F and 71-percent relative humidity
mils		g/hr/m²	g/hr/m²	g/hr/m²
COATING *V-11*				
2.5	S	0.50	0.96	2.52
2.5	W	.49	.91	2.29
5.3	S	.26	.47	1.09
5.2	W	.25	.45	1.02
7.7	S	.18	.34	.80
7.7	W	.22	.36	.81
COATING *E-6*				
2.0	S	.43	----------	2.15
2.0	W	.43	----------	1.92
3.8	S	.27	----------	1.33
3.5	W	.31	----------	1.41
5.7	S	.23	----------	.94
5.6	W	.20	----------	.86
COATING *V-10*				
3.0	S	.32	.62	1.75
3.0	W	.36	.77	1.43
5.9	S	.20	.34	.78
6.0	W	.18	.33	.74
9.0	S	.13	.24	.54
8.9	W	.13	.23	.54
COATING *E-4*				
2.0	S	.35	.66	1.63
2.1	W	.35	.61	1.59
4.0	S	.18	.34	.79
3.9	W	.21	.36	.83
6.3	S	.15	.26	.61
6.3	W	.15	.26	.58
COATING *L-8*				
3.2	S	1.31	2.14	3.82
3.4	W	1.26	2.21	3.69
8.2	S	.60	1.04	1.94
8.2	W	.64	1.08	----------
11.8	S	.38	.65	1.51
11.9	W	.38	.67	----------

5. EFFECT OF WAX FINISH ON THE PERMEABILITY TO MOISTURE OF THE FILMS

Wax is much less permeable to water than the varnishes. This property of waxes is utilized commercially in the coatings of wrapping papers and for the protection of automobile finishes. It has also been found that the leaves and fruits of many plants are covered with a layer of wax which retards the loss of moisture.

The effect of a coating of carnauba wax on the permeability to moisture of aircraft finishes was determined in the course of the present study. Films prepared on amalgamated tin-plate were dipped in an aqueous ammonia solution of this wax and allowed to drain and dry. They were stripped from the plate and tested for moisture perme-

ability by the process outlined above. The results are shown in table 6. The films used were 2 to 3 mils thick and each coating of wax was about 0.2 mil. The additional protection afforded by the thin film of wax against passage of moisture was found to be considerable, being in some cases equivalent to doubling the thickness of the original film.

Carnauba wax is one of the vegetable type and consists largely of fatty acid esters of mono- and dihydric alcohols mixed with the related free acids, alcohols and hydrocarbons. It contains oxygen in the form of hydroxyl groups and ester linkages and has a greater affinity for water, therefore, than the paraffin waxes. These latter materials are nonsaponifiable and consist of mixtures of saturated hydrocarbons.

TABLE 6.—*Effect of wax coating on the permeability to moisture of films of aircraft finishes*

Film thickness	Coats of wax	Relative humidity in cell	Permeability at—		
			70° F and 65-percent relative humidity	85° F and 71-percent relative humidity	100° F and 71-percent relative humidity
mils		%	g/hr/m²	g/hr/m²	g/hr/m²
COATING *V-11*					
2.5	0	100	0.50	0.96	2.52
2.7	1	100	.37	.68	1.49
2.8	2	100	.30	.48	1.21
COATING *V-10*					
3.1	0	0	.42	.97	2.26
3.2	1	0	.32	.69	1.49
3.0	2	0	.25	.55	1.19
3.0	0	100	.32	.62	1.75
3.3	1	100	.29	.49	1.16
3.1	2	100	.23	.42	
COATING *E-4*					
2.0	0	0	.35	.91	1.88
2.2	1	0	.36	.83	1.65
2.7	2	0	.27	.62	1.25
2.0	0	100	.35	.66	1.63
2.3	1	100	.34	.54	1.13
2.5	2	100	.26	.41	.81
COATING *L-8*					
3.2	0	100	1.31	2.14	3.82
3.0	1	100	1.14	1.85	3.37
3.6	2	100	.84	1.69	3.07

V. ABSORPTION OF MOISTURE BY RESINOUS FILMS

The amount of moisture absorbed at various relative humidities by films of glyceryl-phthalate enamel *E-6* and phenol-formaldehyde primer *P-23* was determined by the same method previously used in a study of aircraft fabrics. The results are shown in tables 7 and 8.

TABLE 7.—*Change in weight of glyceryl-phthalate films (E–6) which have been conditioned in air at 21° C and 65-percent relative humidity when they are exposed at other relative humidities*

Relative humidity	Thickness of film	Percentage change in weight on exposure for various periods—								
		Hours			Days		Weeks			6 months
		1	3	6	1	4	1	2	4	
%	mils	%	%	%	%	%	%	%	%	%
0	6	−0.5	−0.9	−1.1	−1.4	−1.5	−1.5	−1.5	−1.5	−1.6
6	6	−.5	−.8	−1.1	−1.2	−1.3	−1.3	−1.3	−1.3	−1.4
33	6	−.2	−.5	−0.6	−0.7	−0.8	−0.8	−0.8	−0.8	−1.0
65	6					−.1	−.2		−.2	−0.3
86	4	.4	.6	.8	.9	.9	.9	.8	.7	.4
94	4	.5	.9	1.1	1.4	1.5	1.5	1.5	1.5	1.0
97	6	.5	.8	1.2	1.7	2.0	2.2	2.7	3.2	4.1
97	4	.7	1.1	1.5	2.0	2.2	2.4	2.9	3.4	4.6
97	2	.9	1.4	1.6	2.1	2.4	2.4	2.9	3.4	4.4
100	4	1.0	1.7	2.2	3.6	5.5	6.0	8.2	11.9	*41.7

* Moisture condensed on film.

TABLE 8.—*Change in weight of phenol-formaldehyde films (P–23) which have been conditioned in air at 21° C and 65-percent relative humidity when they are exposed at other relative humidities*

Relative humidity	Thickness of film	Percentage change in weight on exposure for various periods—								
		hours			days		weeks			6 months
		1	3	6	1	4	1	2	4	
%	mils	%	%	%	%	%	%	%	%	%
0	8	−0.3	−0.4	−0.5	−0.7	−0.8	−0.8	−0.8	−0.8	−0.8
6	8	−.3	−.4	−.5	−.6	−.6	−.6	−.6	−.6	−.8
33	8	−.1	−.2	−.3	−.4	−.4	−.4	−.4	−.4	−.6
65	8					.1	−.1		−.1	−.1
86	8	.1	.2	.3	.4	.4	.4	.4	.3	−.1
94	8	.2	.3	.5	.9	.9	1.0	1.0	1.0	.5
97	8	.2	.5	.7	1.3	1.8	2.1	2.6	3.1	4.8
97	5	.3	.6	.8	1.4	1.9	2.2	2.6	3.1	4.6
97	3	.4	.6	.8	1.3	1.8	2.0	2.4	2.9	4.8
100	8	.3	.6	.9	1.8	3.4	4.2	6.1	9.6	*34.7

* Moisture condensed on films.

It will be noted that the percentage change in weight for both materials at relative humidities of 94 percent or less is practically negligible, being not more than 1.5 percent in any case. Furthermore, equilibrium is practically attained under such conditions after 24 hours. At relative humidities of 97 and 100 percent the absorption of moisture continues over long periods, although in the former case it does not exceed 5 percent. The experiments at 97-percent relative humidity with various thicknesses of films indicate that the final percentage absorption is the same, but that the rate of absorption is somewhat slower for the thicker films.

VI. PERMEABILITY TO MOISTURE OF GELATIN-LATEX GAS-CELL FABRICS

Some observations on the absorption of moisture by gas-cell fabrics were previously reported in this journal.[2, 3] It was believed that information on the permeability of some of these same fabrics would be of value in estimating the amount of moisture which would be transmitted into the cells during periods of high relative humidity.

The gas-cell fabrics which were tested for permeability to moisture are described in table 9, which, except for thickness measurements, is taken from the reference in footnote 3. The fabric designated as *Q39–A–10* contains less gelatin than the standard light-weight fabric *Q39–A–2*, and is hereafter referred to as "improved fabric."

Disks of 72 mm diameter were cut out and sealed to the glass cells by the method previously described. The films were attached with the normally "outside" surface of the fabric exposed to the interior of the cell.

The results obtained at various temperatures and relative humidities are presented in table 10. In order to show a ready comparison between permeability and the amount of paraffin on the fabric, the materials have been listed in table 10 in their order of increasing permeability to moisture. It will be noted that for gas-cell fabrics coated with paraffin, the improved fabric is in every case less permeable to moisture than the standard material. Likewise the paraffin-coated materials are, in general, superior to the fabrics coated with aluminum varnish; this is particularly true for tests at low relative humidity. Under the wet conditions, the painted fabrics were less permeable than certain of the paraffined fabrics; however, the threefold to sixfold greater weight of the paint film corresponding to an increased thickness of coating material must be considered.

TABLE 9.—*Description of gas-cell fabrics studied*

Fabric sample no.	Type of coating	Thickness of coated fabric	Weight of coated fabric	Amount of coating indicated by manufacturer		Total paraffin found
				Inside	Outside	
	GOODYEAR CODE *Q39–A–2* FABRIC					
		mils	oz/yd²	oz/yd²	oz/yd²	oz/yd²
1	Paraffin	7.0	5.41	-------	0.2	0.3
2	----do	7.1	5.66	-------	.4	.6
3	----do	7.4	5.83	0.2	.2	.7
4	----do	7.4	5.96	.2	.4	.8
5	Paraffin and Goodyear code *755C* aluminum paint [a]	7.5	5.94	.2	0.2 paraffin + 0.2 Al paint	[c].6
6	Aluminum powder in flexible spar varnish [b]	8.4	7.30	-------	-------	-------
	GOODYEAR CODE *Q39–A–10* FABRIC					
7	Paraffin	7.1	5.58	-------	0.2	0.35
8	----do	7.2	5.82	-------	.4	.6
9	----do	7.9	6.00	0.2	.2	.8
10	----do	7.8	5.96	.2	.4	.8
11	Paraffin and Goodyear code *755C* aluminum paint [a]	8.0	6.07	.2	0.2 paraffin + 0.2 Al paint	[c].7
12	Aluminum powder in flexible spar varnish [b]	8.4	6.95	-------	-------	-------

[a] The aluminum paint and the flexible spar varnish are apparently of different compositions.
[b] Flexible spar varnish containing aluminum dust is applied to both surfaces. Total weight of coating for sample 6 is 2.2 oz/yd²; for sample 12 is 1.8 oz/yd².
[c] Value may be slightly high as a result of breakdown of the paint coating.

[2] G. M. Kline, J. Research NBS **14**, 67–84 (1935) RP758.
[3] D. F. Houston, J. Research NBS **15**, 163–172 (1935) RP818.

TABLE 10.—*Permeability to moisture of gas-cell fabrics listed in the approximate order of increasing permeability*

Fabric sample no.	Paraffin on fabric	Relative humidity in cell	Permeability at—					
			70° F and 65-percent relative humidity		85° F and 71-percent relative humidity		100° F and 71-percent relative humidity	
	oz/yd²	%	g/hr/m²	g/hr/m²/mm Hg	g/hr/m²	g/hr/m²/mm Hg	g/hr/m²	g/hr/m²/mm Hg
9	0.8	0	0.047	0.004	0.114	0.005	0.47	0.013
11	.7	0	.059	.005	.133	.006	.39	.011
3	.7	0	.063	.005	.141	.006	.55	.016
10	.8	0	.067	.005	.153	.007	.55	.016
4	.8	0	.067	.005	.157	.007	.59	.017
8	[a].6	0	.086	.007	.200	.009	.63	.018
5	.6	0	.106	.009	.255	.012	.86	.025
7	[a].35	0	.110	.009	.263	.012	1.14	.033
2	[a].6	0	.165	.014	.392	.018	1.10	.032
12	0	0	.270	.022	.564	.026	1.37	.039
1	.3	0	.239	.020	.568	.026	1.92	.055
6	0	0	.317	.026	.674	.031	1.10	.032
9	.8	100	.031	.005	.071	.008	.20	.014
10	.8	100	.031	.005	.086	.010	.39	.027
11	.7	100	.039	.006	.090	.010	.24	.017
4	.8	100	.071	.011	.165	.019	.27	.019
5	.6	100	.094	.014	.168	.019	.51	.036
3	.7	100	.102	.015	.212	.024	.39	.027
8	[a].6	100	.188	.028	.341	.038	.86	.060
6	0	100	.235	.036	.404	.045	1.18	.083
12	0	100	.345	.052	.596	.067	1.18	.083
7	[a].35	100	.294	.045	.604	.068	1.45	.101
1	[a].3	100	.353	.053	.819	.092	2.39	.167
2	[a].6	100	.435	.066	.948	.107	1.96	.137

[a] Paraffin on only 1 side of fabric.

Insofar as the effects of temperature and relative humidity on the rate of transmission of moisture through gas-cell fabrics are concerned, the directions of the changes are the same as were observed with paint films. The data in tables 10 and 11 indicate that raising the

TABLE 11.—*Effect of varying relative humidity on the permeability to moisture of paraffined gas-cell fabric*

Fabric sample no.	Relative humidity in cell	Permeability at—			
		70° F and 65-percent relative humidity		100° F and 71-percent relative humidity	
	%	g/hr/m²	g/hr/m²/mm Hg	g/hr/m²	g/hr/m²/mm Hg
3	0	0.063	0.005	0.55	0.016
3	31 to 33	.031	.005	.31	.016
3	75 to 76	.008	.004	.08	.040
3	93	.024	.005	.20	.019
3	100	.102	.015	.39	.027

temperature causes the permeability per unit difference in vapor pressure to increase under both wet and dry conditions, the increase being even greater for the paraffined fabrics than for the paint films. For the fabrics exposed at the lower relative humidity, there is a considerable percentage increase only when the temperature is raised from 85 to 100° F, whereas in saturated water vapor the percentage increase between 70 and 85° F is fairly comparable to that between 85 and 100° F. The anomalous behavior under the dry conditions

cannot be attributed to increase in moisture content of the air, since the percentage increase in moisture content per unit volume in going from 70° F and 65-percent relative humidity to 85° and 71-percent relative humidity is greater than that in going from the latter condition to 100° F and 71-percent relative humidity. It is probable that the difference in the amount of moisture held by the gelatin-latex fabric at the high and low relative humidities is an important factor in the influence of temperature on the moisture permeability.

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